

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: Ditter, et al.
Appl. No.	: 10/603,425
Filed	: June 24, 2003
For	: LAMINATES OF ASYMMETRIC MEMBRANES
Examiner	: Chevalier, A. A.
Group Art Unit	: 1794

ON APPEAL TO THE BOARD OF PATENT APPEALS AND INTERFERENCES
APPELLANT'S BRIEF**Mail Stop Appeal Brief – Patents**

COMMISSIONER FOR PATENTS

P.O. Box 1450

Alexandria, VA 22313-1450

Dear Sir:

The Appellants appeal the rejection of Claims 1, 7, 13-16, 18, 21, 22, 25-27, 29, 30, and 35-44 in the above-referenced patent application. These claims were rejected in a Final Office Action dated June 2, 2009. Appellants filed a Notice of Appeal on November 25, 2009, and an Amendment After Final on November 30, 2009.

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I. REAL PARTY IN INTEREST

Pursuant to 37 C.F.R. 41.37(c)(1), Appellants hereby notify the Board of Patent Appeals and Interferences that the real party in interest is the assignee of record for this application, Pall Corporation, 25 Harbor Park Drive, Suite 1000, Port Washington, New York 11050.

II. RELATED APPEALS AND INTERFERENCES

Appellants are unaware of any other related appeals or interferences.

III. STATUS OF THE CLAIMS

Claims 1, 7, 13-16, 18, 21, 22, 25-27, 29, 30, and 35-44 are finally rejected. Accordingly, Claims 1, 7, 13-16, 18, 21, 22, 25-27, 29, 30, and 35-44 are the subject of this appeal. The claims at issue are attached hereto as Appendix A.

IV. STATUS OF AMENDMENTS

An amendment was submitted on November 30, 2009 subsequent to the June 2, 2009 Final Office Action. Appellants respectfully request entry of the Amendment After Final as the amendments to the specification presented therein have been made to comply with a requirement of form expressly set forth in the previous action, namely, the objection to the specification. The claims have not been amended in response to the June 2, 2009 Final Office Action.

V. SUMMARY OF THE CLAIMED SUBJECT MATTER

The claimed subject matter is directed to composite filters and methods for preparing same. More specifically, it is directed to filter laminates of multiple discrete layers of material bonded together, with at least one of the layers being an asymmetric membrane. *See* Specification, page 1, lines 12-14. In one embodiment, a filter laminate comprising a plurality of discrete layers of material is provided, the layers including a first membrane, a second membrane, and a bond therebetween. The first membrane can be an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface are larger than pores of the skin surface (*see* Specification, page 9, lines 13-17), and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface (*see*

Specification, page 12, lines 27-29); a second membrane, wherein said second membrane is an asymmetric membrane having a skin surface and an open surface (*see* Specification, page 9, lines 13-17), wherein pores of the open surface are larger than pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface (*see* Specification, page 12, lines 27-29); and a bond between the membranes (*see* Specification, page 9, lines 11-13). The bond can be between the skin surface of the first membrane and the skin surface of the second membrane (*see* Specification, page 9, lines 25-27), wherein the filter laminate has a higher bubble point than either the first membrane or the second membrane, wherein a bubble point of the filter laminate is greater than a bubble point of the first membrane layer and the second membrane layer in a skin-to-skin configuration without bonding (*see* Specification, page 10, lines 4-11), and wherein the filter laminate has a greater integrity than a combination wherein the skin surface of the first membrane and the skin surface of the second membrane are adjacent to each other but not bonded to each other (*see* Specification, page 10, line 29 to page 11, line 4), wherein the filter laminate has a flow rate therethrough such that the filter laminate is configured for separation by filtration (*see* Specification, page 9, lines 5-7). Alternatively, the bond can be between the skin surface of the first membrane and the open surface of the second membrane (*see* Specification, page 9, lines 25-27).

VI. GROUND S OF REJECTION TO BE REVIEWED ON APPEAL

- A. The Examiner has rejected pending Claims 39-41 under 35 U.S.C. §103(a) as being unpatentable over U.S. Patent No. 4,280,909 ("Deutsch"). See Final Office Action dated June 2, 2009, pages 3-4.
- B. The Examiner has rejected pending Claims 7, 13-16, 18, 21, 22, 25, 29, 30, 35-39, and 42-44 as being unpatentable over U.S. Patent No. 5,236,588 ("Zhang"). See Final Office Action dated June 2, 2009, pages 4-8.
- C. The Examiner has rejected pending Claims 1, 26, and 27 as being unpatentable over Zhang in view of U.S. Patent No. 4,906,371 ("Miller"). See Final Office Action dated June 2, 2009, pages 8.

VII. APPELLANTS' ARGUMENT

A. Rejection of Claims 39-41 over Deutsch

On page 3, the Office Action states Deutsch discloses a filter laminate (col. 6, line 25) comprising a plurality of discrete layers of material (col. 4, lines 9-11 and figure 1), wherein each layer is adjacent to at least one other layer (figure 1). The Office Action further states that Deutsch discloses a bond between the skin surface of the first membrane and the open surface of the second membrane (col. 5, lines 9-11 and figure 1). Appellants respectfully disagree.

(1) The Office Action does not establish a *prima facie* case of obviousness

It is well settled that the Examiner "bears the initial burden of presenting a *prima facie* case of unpatentability..." *In re Sullivan*, 498 F.3d 1345 (Fed. Cir. 2007). Until the Examiner has established a *prima facie* case of obviousness, the Applicant need not present arguments or evidence of non-obviousness. To establish a *prima facie* case of obviousness, the Examiner must establish at least three elements. First, the prior art reference (or references when combined) must teach or suggest all of the claim limitations: "All words in a claim must be considered in judging the patentability of that claim against the prior art." *In re Wilson*, 424 F.2d 1382, 165 U.S.P.Q. 494, 496 (CCPA 1970); *see also M.P.E.P. § 2143.03*. Second, there must be a reasonable expectation of success. *In re Merck & Co., Inc.*, 800 F.2d 1091 (Fed. Cir. 1986); *see also M.P.E.P. § 2143.02*. And finally, the Examiner must articulate some reason to modify or combine the cited references that renders the claim obvious. Merely establishing that the claimed elements can be found in the prior art is not sufficient to establish a *prima facie* case of obviousness:

As is clear from cases such as *Adams*, a patent composed of several elements is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art. *KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1741 (2007) (emphasis added).

Instead, the Court has made clear that the Examiner must establish a reason one of skill in the art would have combined the elements of the prior art, and that such reason must be more than a conclusory statement that it would have been obvious.

Often, it will be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was an apparent

reason to combine the known elements in the fashion claimed by the patent at issue. To facilitate review, this analysis should be made explicit. *See In re Kahn*, 441 F.3d 977, 988 (C.A.Fed.2006) (“[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness”). *KSR Int’l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1740-1741 (2007). (original emphasis).

Deutsch does not teach or fairly suggest all of the limitations of Claims 39-41, namely Deutsch does not disclose a filter laminate, much less a bond between the skin surface of the first membrane and the open surface of the second membrane. As is clear from a reading of the present application, the term “laminate” refers to layers of material joined by a bond “formed by application of heat and/or pressure” (*see* Specification, page 13, lines 15-18). Details regarding the temperature, pressure, and tension conditions of the lamination process are provided in the Specification, at page 14, line 27 to page 15. The layers are “subjected to conditions sufficient to achieve a laminate, typically by application of heat” (*see* Specification, page 16, lines 1-2). In contrast, Deutsch discloses a microporous member “formed by clamping together three pieces of sheeting” (*see* col. 4, lines 9-11 and lines 34-36). Clamps are the only means taught by Deutsch to fasten filters together (*see* col. 6, Example I and cols. 6-7, Example 2). While the “edges of the stack of filters” are disclosed as being “sealed fluid tight with three coats of commercial epoxy type cement” (col. 6, lines 51-53), the adjacent porous surfaces of the filter layers themselves are not bonded together, they are merely placed adjacent to each other without a bond between the surfaces, with the clamp holding the layers in place.

Accordingly, Deutsch does not teach or fairly suggest all limitations of pending Claim 39, namely a “filter laminate” and “a bond between the skin surface of the first membrane and the open surface of the second membrane,” such that a *prima facie* case of obviousness cannot be established. Since dependent claims are necessarily narrower than the independent claim, a *prima facie* case of obviousness cannot be made against Claims 40 and 41, which depend from pending Claim 39. For at least these reasons, Appellants respectfully request reversal of the rejection.

B. Rejection of Claims 7, 13-16, 18, 21, 22, 25, 29, 30, 35-39, and 42-44 over Zhang.

On page 4, the Office Action states Zhang discloses a filter laminate (col. 4, line 23) comprising a layer of material with two zones (Figure 4) wherein each zone is adjacent at least one other zone, and wherein the zones comprise a first and second membrane, wherein each

membrane is an asymmetric membrane of material (Figure 4). The Office Action further states that "Zhang fails to disclose a plurality of discrete layers. Furthermore, Applicant's specification is silent as to with regard to the plurality of 'discrete' layers. Therefore, since applicant does not appear to disclose criticality to the process of having "discrete" layers the single layer with dual zones of Zhang is deemed to be equivalent ... to Applicant's claimed plurality of 'discrete' layers, since the resulting structure in both is a filter with a first and second membrane ... and a bond between the open surface of the first membrane and the open surface of the second membrane" (Office Action, page 4, last paragraph, continuing to page 5). Appellants respectfully disagree.

(1) The Office Action does not establish a *prima facie* case of obviousness

The criteria for establishing a *prima facie* case of obviousness are set forth above. Zhang does not teach or fairly suggest all of the limitations of Claims 7, 13-16, 18, 21, 22, 25, 29, 30, 35-39, and 42-44, namely Zhang does not disclose a filter laminate, much less a first membrane and a second membrane with a bond between ... the first membrane and ... the second membrane, as recited in each of pending independent Claims 21, 39, and 42. As discussed above in regard to the rejection over Deutsch, is clear from application, the term "laminate" refers to layers of material joined by a bond "formed by application of heat and/or pressure" (see Specification, page 13, lines 15-18). Details regarding the temperature, pressure, and tension conditions of the lamination process are provided in the Specification, at page 14, line 27 to page 15. The layers are "subjected to conditions sufficient to achieve a laminate, typically by application of heat" (see Specification, page 16, lines 1-2). In contrast, Zhang merely discloses various asymmetric polymer membranes. Contrary to the Examiner's assertion, Figure 4 does not depict two membranes – it depicts a pore size distribution for a single membrane wherein "there is a layer of pores having the smaller relative diameters at the middle of the membrane, and in which the pore diameters increase continuously or discontinuously from both sides of the middle pore layer to the surfaces of the membranes." There is no teaching or suggestion in Zhang as to laminating together any of the disclosed membranes, or forming any other sort of bond between two membranes.

As to the Examiner's assertion that "the single layer with dual zones of Zhang is deemed to be equivalent ... to Applicant's claimed plurality of 'discrete' layers," the Examiner is improperly disregarding the limitations of "a first membrane", "a second membrane", and "a bond between ... the first membrane and ... the second membrane." All words in a claim must be

considered in judging the patentability of that claim against the prior art. *In re Wilson*, 424 F.2d 1382, 1385, 165 USPQ 494, 496 (CCPA 1970). Moreover, the Examiner's conclusion that Appellants' filter laminate is equivalent to Zhang's asymmetric membrane associated in Figure 3 is improperly based on Appellants' disclosure, as no art is cited disclosing Appellants' claimed filter laminate. In order to rely on equivalence as a rationale supporting an obviousness rejection, the equivalency must be recognized in the prior art, and cannot be based on applicant's disclosure or the mere fact that the components at issue are functional or mechanical equivalents. *In re Ruff*, 256 F.2d 590, 118 USPQ 340 (CCPA 1958).

Accordingly, Zhang does not teach or fairly suggest all limitations of pending Claims 21, 39, and 42 namely a "filter laminate" and "a bond between ... the first membrane and ... the second membrane," such that a *prima facie* case of obviousness cannot be established. Since dependent claims are necessarily narrower than the independent claim, a *prima facie* case of obviousness cannot be made against Claims 7, 13-16, 18, 22, 25, 29, 30, 35-38, 43, and 44, which variously depend from the pending independent claims. For at least these reasons, Appellants respectfully request reversal of the rejection.

C. Rejection of Claims 1, 26, and 27 over Zhang in view of Miller.

On page 7, the Office Action states Zhang fails to disclose a laminate comprising a hot melt adhesive layer. The Examiner cites Miller as disclosing "bonding the membrane to additional layers with a solventless hot melt adhesive, such that it does not have a low melt temperature that it will not adhesively function at typical heat sterilization and autoclave temperatures (col. 12, lines 40-51)".

(1) The Office Action does not establish a *prima facie* case of obviousness

The criteria for establishing a *prima facie* case of obviousness are set forth above. Claims 1, 26 and 27 each depend from independent Claim 21. Claims 1 and 26 both recite a hot melt adhesive. Claim 27 recites a low melting component that melts and forms a bond. The criteria for establishing a *prima facie* case of obviousness are set forth above. The Examiner proposes to combine the teachings of Miller relating to lamination of membranes with those of Zhang, which merely discloses various types of asymmetric membranes. Miller discloses a filter element incorporating a microporous membrane having an elongated porous filtration area bordered by substantially non-porous sealing areas of non-porous tape heat sealed to the membrane (see col. 12, ll. 3-6). The tape is a polymeric tape which is non-porous (emphasis

added, *see* col. 12, ll. 55-59). Accordingly, in Miller, the membrane has two distinct types of regions: 1) porous filtration areas comprising layers that are adjacent to each other but not bonded to each other (non-laminated areas), through which filtration takes place; and 2) non-porous regions where layers are bonded to each other by a non-porous heat sealable tape (laminated areas), which results in a non-porous bond through which no filtration takes place. The use of a non-porous sealing (bonding) layer is critical in the filters of Miller, and Miller distinguishes his sealing methods from those of the prior art based on this non-porous sealing layer: "in most of the prior art uncovered by applicant relating to sealing filters, the filter media sealing area is porous, so that when a thermoplastic or sealing surface is applied thereto it flows through the porous media to effect the seal." *See* col. 7, ll. 24-28. Appellant notes that Miller includes no teaching or suggestion of bonding in filtration areas, only in sealing areas.

If the teachings of Zhang and Miller were combined as suggested by the Examiner, using the non-porous sealing tape of Miller to bond together two membrane layers across their entire surface area would yield a laminate unsuitable for use as a filtration media because the laminate would be non-porous – no liquid could pass through it. Likewise, if only an outer sealing portion of two membrane layers were laminated, and not the remaining portion used for filtration, the filtration portions would not be laminated and the full benefits of lamination as described in Appellants' specification as filed would not be achieved (*see* page 11, ll. 17-19 "[i]f the membranes are not laminated together, there is a chance that they can separate during packaging into cartridges, during filtration, and/or during integrity testing."). To establish a *prima facie* case of obviousness, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. However, if the proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose, then there is no suggestion or motivation to make the proposed modification. *In re Gordon*, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984). The proposed modification of Zhang by Miller would result in a laminate unsuitable for use as a filter because it is non-porous, or a filter where the portions through which liquid is filtered are not laminated.

With respect to Claims 26 and 27, Miller only discloses a non-porous heat sealable tape. There is no teaching of a web hot melt adhesive, or bicomponent fibers containing both a low melting component and a high melting component, wherein the low melting component melts

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and forms a bond at a temperature at which the high melting component, the first membrane, and the second membrane survive unchanged.

Accordingly, Zhang in view of Miller cannot be combined so as to yield the filter laminate as recited in Claims 1, 26, and 27. A *prima facie* case of obviousness therefore cannot be established. For at least these reasons, Appellants respectfully request reversal of the rejection.

D. Conclusion

In view of the arguments presented above, Appellants submit that Claims 1, 7, 13-16, 18, 21, 22, 25-27, 29, 30, and 35-44 are allowable. Appellants therefore respectfully request that the Board reverse the rejections of the pending claims as unpatentable under 35 U.S.C. §103(a).

Please charge any additional fees, including any fees for additional extension of time, or credit overpayment to Deposit Account No. 11-1410.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: 12/1/09

By: 

Rose M. Thiessen
Registration No. 40,202
Attorney of Record
Customer No. 20995
(619) 235-8550

VIII. APPENDIX A – CLAIMS ON APPEAL

1. (Previously presented) The filter laminate of Claim 21, wherein the bond is a hot melt adhesive heat-bonded to said skin surface of said first membrane and to said skin surface of said second membrane.

2-6. (Canceled)

7. (Previously presented) The filter laminate of Claim 21, wherein said asymmetric region of at least one of said first membrane and said second membrane comprises a reticular network of flow channels.

8-12. (Canceled)

13. (Previously presented) The filter laminate of Claim 21, further comprising a third membrane.

14. (Previously presented) The filter laminate of Claim 13, further comprising a bond between the third membrane and either the first membrane or the second membrane, wherein the bond between the third membrane and either the first membrane or the second membrane is a hot melt adhesive heat-bonded to said third membrane and either the first membrane or the second membrane.

15. (Previously presented) The filter laminate of Claim 21, wherein said first membrane and said second membrane comprises a polymer selected from the group consisting of polyvinylidene fluoride, polyarylsulfone, polyethersulfone, polyamides, and cellulosic derivatives.

16. (Previously presented) The filter laminate of Claim 1, further comprising a layer comprising a material selected from the group consisting of polyester, polypropylene, polyolefin, polyethylene, nylon, paper, cellulose, glass fiber, and acrylic.

17. (Canceled)

18. (Original) The filter laminate of Claim 16, wherein said material is selected from the group consisting of nonwoven fibrous material, woven fibrous material, web material, sheet material, calendared material, wet laid material, dry laid material, and extruded material.

19-20. (Canceled)

21. (Previously presented) A filter laminate, comprising:

a plurality of discrete layers of material, wherein each layer is adjacent to at least one other layer, said plurality of discrete layers comprising:

a first membrane, wherein said first membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface are larger than pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface;

a second membrane, wherein said second membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface are larger than pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface; and

a bond between the skin surface of the first membrane and the skin surface of the second membrane, wherein the filter laminate has a higher bubble point than either the first membrane or the second membrane, wherein a bubble point of the filter laminate is greater than a bubble point of the first membrane layer and the second membrane layer in a skin-to-skin configuration without bonding, and wherein the filter laminate has a greater integrity than a combination wherein the skin surface of the first membrane and the skin surface of the second membrane are adjacent to each other but not bonded to each other, wherein the filter laminate has a flow rate therethrough such that the filter laminate is configured for separation by filtration.

22. (Previously presented) The filter laminate of Claim 21, wherein the bond is formed from a nonwoven fibrous material, a woven fibrous material, or an open extruded material.

23-24. (Canceled)

25. (Previously presented) The filter laminate of Claim 21, wherein the filter laminate is permeable to water.

26. (Previously presented) The filter laminate of Claim 21, wherein the bond is a web hot melt adhesive.

27. (Previously presented) The filter laminate of Claim 21, wherein the bond comprises bicomponent fibers containing both a low melting component and a high melting component, wherein the low melting component melts and forms a bond at a temperature at which the high melting component, the first membrane, and the second membrane survive unchanged.

28. (Canceled)

29. (Previously presented) The filter laminate of Claim 21, wherein the first membrane and the second membrane have different skin pore sizes.

30. (Previously presented) The filter laminate of Claim 21, wherein the first membrane and the second membrane have same skin pore sizes.

31-34. (Canceled)

35. (Previously presented) The filter laminate of Claim 21, wherein, for at least one of the first membrane and the second membrane, said pores of said open surface have an average diameter at least about 5 times greater than an average diameter of said pores of said skin surface.

36. (Previously presented) The filter laminate of Claim 21, wherein, for at least one of the first membrane and the second membrane, said pores of said open surface have an average diameter at least about 10 times greater than an average diameter of said pores of said skin surface.

37. (Previously presented) The filter laminate of Claim 35, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is from about 0.01 μm to about 10.0 μm .

38. (Previously presented) The filter laminate of Claim 35, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is less than about 0.01 μm .

39. (Previously presented) A filter laminate, comprising:
a plurality of discrete layers of material, wherein each layer is adjacent at least one other layer, said plurality of discrete layers comprising:

a first membrane, wherein said first membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface have an average diameter at least about 5 times greater than an average

diameter of pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface;

a second membrane, wherein said second membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface have an average diameter at least about 5 times greater than an average diameter of pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface; and

a bond between the skin surface of the first membrane and the open surface of the second membrane, wherein an average pore size of the pores of the open surface of the first membrane is larger than an average pore size of the pores of the open surface of the second membrane, wherein the filter laminate has a flow rate therethrough such that the filter laminate is configured for separation by filtration.

40. (Previously presented) The filter laminate of Claim 39, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is from about 0.01 μm to about 10.0 μm .

41. (Previously presented) The filter laminate of Claim 39, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is less than about 0.01 μm .

42. (Previously presented) A filter laminate, comprising:
a plurality of discrete layers of material, wherein each layer is adjacent at least one other layer, said plurality of discrete layers comprising:

a first membrane, wherein said first membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface have an average diameter at least about 5 times greater than an average diameter of pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface;

a second membrane, wherein said second membrane is an asymmetric membrane having a skin surface and an open surface, wherein pores of the open surface have an average diameter at least about 5 times greater than an average diameter of pores of the skin surface, and wherein said asymmetric region comprises flow channels that gradually increase in diameter from said skin surface to said open surface; and

a bond between the open surface of the first membrane and the open surface of the second membrane, wherein the filter laminate has a flow rate therethrough such that the filter laminate is configured for separation by filtration.

43. (Previously presented) The filter laminate of Claim 42, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is from about 0.01 μm to about 10.0 μm .

44. (Previously presented) The filter laminate of Claim 42, wherein, for at least one of the first membrane and the second membrane, an average diameter of said pores of said skin surface is less than about 0.01 μm .

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IX. APPENDIX B – EVIDENCE

Attached hereto is a copy of the evidence cited in Appellants' Brief. The list of evidence below is accompanied by a statement setting forth where in the record that evidence was entered into the record by the Examiner.

Item	Reference	Entered
1	U.S. Patent No. 4,280,909 to Deutsch	Cited by the Examiner in the Office Action dated June 2, 2009
2	U.S. Patent No. 5,236,588 to Zhang	Cited by the Examiner in the Office Action dated June 2, 2009
3	U.S. Patent No. 4,906,371 to Miller	Cited by the Examiner in the Office Action dated June 2, 2009

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X. APPENDIX C – RELATED PROCEEDINGS

None – there are no decisions rendered by a court or the Board in any related proceedings identified above.

[54] MICROPOROUS MEMBER WITH INTERCONNECTED, ORIENTED TAPERED VOIDS

[76] Inventor: Daniel H. Deutsch, 141 Kenworthy Dr., Pasadena, Calif. 91105

[*] Notice: The portion of the term of this patent subsequent to Apr. 3, 1996, has been disclaimed.

[21] Appl. No.: 38,586

[22] Filed: May 14, 1979

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 910,110, May 30, 1978, abandoned.

[51] Int. Cl.³ B01D 31/00; B01D 53/22

[52] U.S. Cl. 210/490; 210/500.2;

55/158; 417/572

[58] Field of Search 210/500 M, 321 R, 433 M, 210/504, 489, 490, 491; 55/158, 485, 487; 417/572; 264/109, 128; 156/644, 668

[56] References Cited

U.S. PATENT DOCUMENTS

Re. 29,524 1/1978 Spencer 428/134
3,158,532 11/1964 Poll et al. 210/504

3,276,996 10/1966 Lazarc 210/500 M
3,749,646 7/1973 Pirt 210/22
3,764,018 10/1973 Shaw et al. 210/500 M
3,770,532 11/1973 Bean et al. 156/7
3,839,201 10/1974 Miller 210/22
3,988,245 10/1976 Wang 210/500 M
4,026,977 5/1977 Bourgaud 264/41
4,097,383 6/1978 Ohtani et al. 210/500 M
4,119,418 10/1978 Smid 55/158
4,147,481 4/1979 Deutsch 417/572

OTHER PUBLICATIONS

"Membrane Ultrafiltration", Porter et al., Chem. Tech., Jan., 1971.

Primary Examiner—Charles N. Hart
Assistant Examiner—David R. Sadowski
Attorney, Agent, or Firm—Lyon & Lyon

[57]

ABSTRACT

A microporous member for causing the circulation of a fluid therethrough. The microporous member is permeated by numerous sequentially interconnected oriented generally tapered voids. The microporous member and a fluid form a system wherein the fluid is urged through the microporous member. The microporous member is useful in causing the circulation of fluids.

4 Claims, 12 Drawing Figures

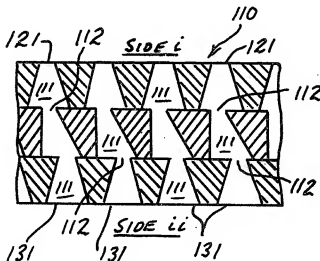


FIG. 1.

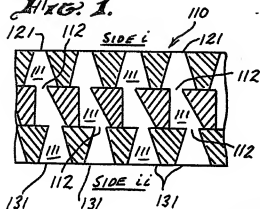


FIG. 2.

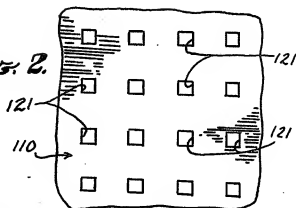


FIG. 3.

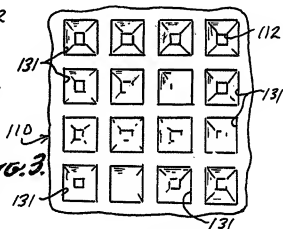


FIG. 4.

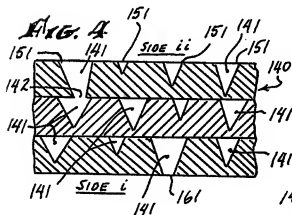


FIG. 5.

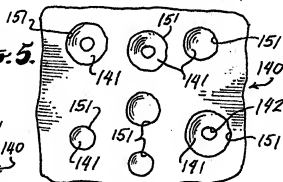
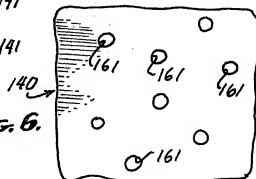
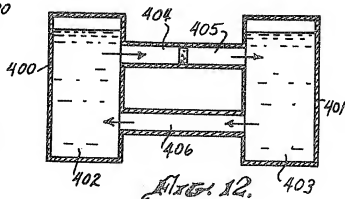
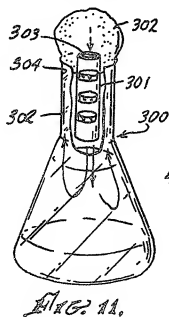
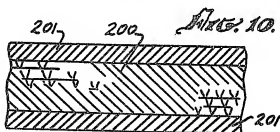
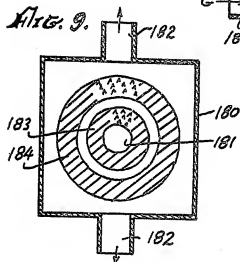
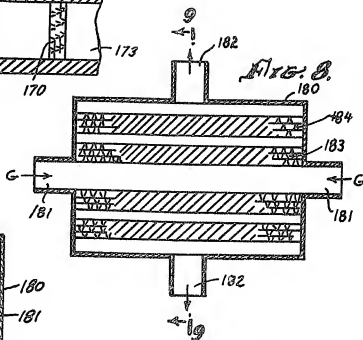
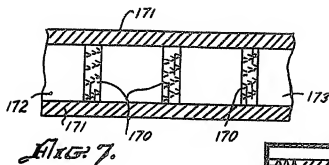


FIG. 6.





MICROPOROUS MEMBER WITH INTERCONNECTED, ORIENTED TAPERED VOIDS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 910,110 filed May 30, 1978 now abandoned.

BACKGROUND OF THE INVENTION

The circulation of fluids through open and closed systems has many applications in the arts, sciences and technology. Mechanical reciprocating pumps, centrifugal pumps, undulating tubes, thermal gradients and fans are all commonly used to move fluids. One particular application where the above listed circulating systems are often impractical is in bacteriological research where a sterile flask has a plug of cotton or other porous substance in the neck thereof and ambient air or other gas is allowed to pass through the cotton. For many reactions such as fermentation reactions the rate at which the air passes through the cotton is an important factor which determines the rate at which the reaction takes place.

A major shortcoming of the use of a cotton plug in the sterile shake flask is the very slow rate of gas exchange through the cotton plug. Consequently, the gas exchange through the cotton plug is rate limiting rather than the biological process in the bacteriological medium. Elaborate sterile gas pumping systems have been developed and used to increase the rate of air throughput. However, such systems are quite expensive, difficult to operate and maintain and provide a source of possible contamination. Some bacteriological processes are carried out under reduced pressure or elevated pressure and reactions are also carried out in the presence of a particular gas.

More particularly, the forced flow of gases has typically utilized mechanical compressors or other devices which can give rise to impurities caused by the necessary presence of lubricants. The need for moving gases in highly purified conditions has made most mechanical systems impractical. Furthermore, many gases are not compatible with the common materials of construction and thus can not be pumped by conventional devices. Still further, some processes require elevated temperatures or reduced temperatures. The design of systems for circulating air or other gases is made more difficult by the presence of such conditions.

Before gases used or generated in industrial processing may be discharged into the atmosphere, the gases are required, by law, to be depolluted of objectionable substances. A large part of the cost involved in the depollution process stems from the cost of physically moving the gases through complex systems.

The movement of solvents and solutes through semipermeable membranes has been studied extensively. The phenomena of reverse osmosis through a membrane is used in the desalination of sea water and other liquid purification processes.

When a solution, U, of solute, X in solvent Y, is placed on one side of a semipermeable membrane, M, which is permeable to the solvent, Y, but impermeable to the solute, X, and the pure solvent, Y, is placed on the other side of this semipermeable membrane, M, then an

osmotic pressure, P_o , develops in the solution U, such that:

$$P_o = cRT$$

EQ. (1)

Where "c" is the molar concentration of the solute X in the solution U; R is the universal gas constant and T is the absolute temperature. This equation for osmotic pressure was proposed by van't Hoff in 1887.

In the above model, when the solution, U, and the pure solvent, Y, exert the same hydrostatic pressure on the membrane, M, the differential external pressure on the membrane P_e is zero, and the osmotic pressure, P_o , generated in this system produces a net flow rate, J_o , of the solvent, Y, from the side containing the pure solvent through the semipermeable membrane into the side holding the solution, U, of solute, X, in solvent, Y. J_o is the net flow rate of liquid through the membrane when the differential external pressure on the membrane, P_e , is zero.

In the above model, if a differential external pressure on the membrane, P_e , is exerted through the solution, U, such that P_e is greater than the osmotic pressure, P_o , then the pure solvent, Y, will flow in the reverse direction, from the solution, U, side of the semipermeable membrane into the pure solvent side of the semipermeable membrane. Large scale practical application of this is made in reverse osmosis where pure water is obtained from salt water by the use of a semipermeable membrane, pervious to water but impervious to salt. A very general interrelationship, characteristic of transport phenomena in general during irreversible thermodynamics, for fluxes, forces and their phenomenological coefficients was developed by L. Onsager.

In many instances it is desired to move a fluid (whether it be a gas or a solution) in which there is no concentration difference across the path of flow. In such cases no osmotic pressure, P_o , exists. A system is thus needed which will move fluids where there is no concentration or composition change along the flow path.

SUMMARY OF THE INVENTION

It is thus an object of the present invention to provide a microporous member, which is simple to use, inexpensive to maintain and yet effective to cause the flow of certain fluids therethrough. When said microporous member is installed in a conduit, chamber or other container and the said conduit, chamber or other container is filled with certain fluids, the said microporous member will urge the said fluid to flow through the conduit, chamber or other container.

It is another important object of the present invention to provide a gas-urging microporous member, useful for depolluting industrial smoke stack gases.

It is a still further object of the present invention to provide a gas-urging microporous member which consumes no energy.

It is another important object of the present invention to provide a solution-urging microporous member, useful for depolluting polluted industrial liquid waste solutions.

It is a still further object of the present invention to provide a solution-urging microporous member which consumes no energy.

The present invention is for a microporous member fabricated from a relatively fluid impermeable material, and generally having two opposing surfaces in its sim-

plest forms such as a sheet or a hollow tube. Between the two opposite surfaces of the microporous member are numerous generally tapered voids, interconnected with ports, wherein substantially all of the generally tapered voids are oriented with their apexes directed toward one of the surfaces of the microporous member and substantially all of the bases of the generally tapered voids are directed toward the opposite surfaces of the said microporous member. A fluid can pass through the said microporous member only by flowing through the generally tapered voids and the interconnecting ports. On the average, any particular particle present in the fluid will have to pass sequentially through at least three interconnected generally tapered voids on passing from the first surface of the microporous member, through the microporous member, to the second surface of the microporous member.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary cross-sectional side elevation of a portion of the microporous member of the present invention.

FIG. 2 is a top plan elevation of the portion of the microporous member of FIG. 1.

FIG. 3 is a bottom plan elevation of the portion of the microporous member of FIG. 1.

FIG. 4 is a fragmentary cross-sectional side elevation of a portion of a microporous member of the present invention having irregularly spaced voids.

FIG. 5 is a top plan view of the portion of the microporous member of FIG. 4.

FIG. 6 is a bottom plan view of the portion of the microporous member of FIG. 5.

FIG. 7 is a cross-sectional side elevation of a conduit having three microporous members of the present invention positioned therein.

FIG. 8 is a cross-sectional side elevation of a conduit having two tubular microporous membranes of the present invention positioned therein.

FIG. 9 is a cross-sectional view taken along line 9-9 of FIG. 8.

FIG. 10 is a fragmentary cross-sectional side elevation of a portion of the microporous member of the present invention supported by an inert member.

FIG. 11 is a cross-sectional side view of a flask having a conduit with three microporous members positioned therein.

FIG. 12 is a cross-sectional side elevation of a microporous member mounted in one of two conduits connecting two tanks filled with a solution.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The cross-sectional view through the microporous member 110 in FIG. 1 is illustrative of the microstructure present in the microporous member of this invention. The generally tapered voids 111 are all aligned so that each of their apexes are directed towards side i and each of their bases are directed towards side ii. The ports 112 interconnect the oriented voids 111. The generally tapered voids, while not all exactly identical in size and shape are approximately identical, are located in a regular square array. The top surface, side i, is shown in FIG. 2 where 121 are the openings in the microporous member 110. The bottom surface, side ii, is shown in FIG. 3 where 131 are the larger openings in the microporous member 110.

The term "tapered" is intended to include shapes such as "conical" and "pyramidal" and such shapes include those which have for their base a plane triangle, rectangle, or other polygon and for their sides several triangles with a common vertex and with their bases forming the sides of the base. The polygon base may have a very large number of sides and may even be curved in a portion or all of its sides.

The microporous member depicted in FIGS. 1-3 can be formed by clamping together three pieces of sheeting cut from a single piece of sheeting wherein the sheeting is perforated in a uniform square array by tapered holes of approximately the same size and shape, and wherein before being clamped together the tapers are oriented to point in the same direction and the holes are aligned so that they fall one on top of another. (The clamping mechanism is not shown in FIGS. 1-3.)

The cross-section view through the microporous member 140 in FIG. 4 is illustrative of the microstructure present in the microporous member of the present invention. The generally tapered voids 141 are conical and all aligned so that each of their apexes are directed towards side i and each of their bases are directed towards side ii. The ports 142 interconnect the oriented voids 141. The generally tapered voids, while not exactly identical in size and shape are approximately identical, are located in a regular array perpendicular to the surfaces of the microporous member and in a regular array parallel to the surfaces of the microporous member. The top surfaces, side i, is shown in FIG. 5 where 151 are the openings in the microporous member 140. The bottom surface, side ii, is shown in FIG. 6 where 161 are the openings in the microporous member 140.

The microporous member depicted in FIGS. 4-6 can be formed by sealing together three pieces of sheeting cut from a single piece of sheeting wherein the sheeting is perforated in a random array by tapered holes of approximately the same size and shape. In this case not all the voids will interconnect the two surfaces.

The microporous member depicted in FIGS. 4-6 can be formed by clamping together three pieces of sheeting cut from a single piece of sheeting wherein the sheeting is perforated in a random array by tapered holes approximately the same size and shape. In this case not all the voids will interconnect the two surfaces. (The clamping mechanism is not shown in FIGS. 4-6.)

The microporous member can be sealed, gas tight, inside a gas impervious conduit. Three such oriented microporous members, 170 are shown in FIG. 7 sealed in a conduit 171. The three microporous members, 170, in FIG. 7 are oriented so that the apexes of the generally tapered voids are all pointed in the same general direction towards exit ports 173, FIG. 7. In the atmosphere of a gas, G, under specified temperature and pressure and wherein the effusional resistance coefficient, ξ , defined below, of the unit as a whole, between the entrance port 172 and the exit port 173, is greater than 10^{-4} and less than 2.0, the said gas, G, is urged through the conduit from port 172 to port 173.

The microporous member, in the form of tubes, 183 and 184 can be mounted in a gas tight chamber 180 as shown in FIG. 8. The entrance ports for the gas, G, are shown as 181 and the corresponding exit ports are 182. Two concentric tubes of the microporous member, 183 and 184, oriented so that the apexes of the generally pyramidal voids are directed outward from the central axis of the tubes are sealed gas tight into the said chamber.

An alternate cross-sectional view of the chamber shown in FIG. 8 is depicted in FIG. 9.

The microporous member 200 of FIG. 10 is shown supported by two coarse porous glass members 201.

The use of three microporous members, mounted in a conduit as shown in FIG. 7, is shown in FIG. 11 where it is used in the neck of a bacteriological flask 300. The bacteriological flask 300 holds the three microporous members mounted in the conduit 301. A wad of cotton 302 holds the conduit 301 in place and maintains the sterility. Air enters at 303, is urged through the conduit 301 by the microporous members, passes into the flask and then out at 304.

A microporous member mounted in a conduit as part of a solution circulating system is depicted in FIG. 12. Two tanks, 400 and 401 are connected by two conduits 404 and 406, and a microporous member 405 is sealed, solution tight, into conduit 404 such that substantially all of the apexes of the generally pyramidal voids permeating the microporous member are directed toward tank 401. The tanks 400 and 401, and the conduits 404 and 406 are filled with a solution U of the solute S in the solvent Y. Under zero external pressure, P_0 , the solution U is urged through the microporous member 405 and thus the solution U is circulated between the two tanks in the directions indicated by the arrows.

If the solutions 402 and 403 in the tanks 400 and 401 respectively were held at different temperatures, the unit depicted in FIG. 12 would act as a heat transfer device, effectively transferring heat from the hotter tank to the colder tank. Such heat transfer devices find extensive use in various technologies such as nuclear energy and the chemical processing industry.

The microporous member, permeated by numerous sequentially interconnected generally tapered voids, wherein essentially all the generally tapered voids are similarly oriented and closely aligned, can be formed into a wide variety of shapes depending upon the specific requirements of a particular application. This invention, as herein described, is intended to cover only the basic microscopic structure making up the microporous member and not any specific shape or configuration into which the microporous member might be fabricated. Thus the microporous member could, among others, be in the form of a thin sheet, a plate, a rod, a hollow tube, a tube closed at one end, a hollow sphere, or a hollow box, to mention but a few of the possible forms.

It is contemplated that while three sequentially connected generally tapered voids may be used in some cases in general a much larger number will be employed such as 50, 700, 40,000 or even 100,000,000. In all cases a substantial majority of the apexes of the generally tapered voids are directed toward one of the surfaces of the microporous member and the corresponding bases of the generally tapered voids are directed towards the opposite surface of the microporous member.

It is further contemplated that two or more microporous members can be used in series whereby the effect of one microporous member is augmented by additional microporous members.

The microporous member is greater than 0.001 micron in thickness and less than 100 centimeters in thickness.

The dimensions of the generally tapered voids constitute an important part of this invention. The average distance across the base of the generally tapered void is greater than 0.001 micron and is less than 100 microns.

The average angle at the apex of the generally tapered void is greater than about 10° and less than about 160° . The average distance across the ports interconnecting the generally tapered voids is greater than 0.0002 micron and less than 100 microns. On the average, each generally tapered void will have at least two and less than 16 ports interconnecting it with other generally tapered voids.

The average density of asymmetric pores through the microporous member is greater than about 10 per square centimeter and limited only by the loss of structural integrity on the high side. Densities of the order of 10^{14} per square centimeter are contemplated.

The microporous member of this invention can be fabricated from a very wide variety of materials such as, but not limited to, plastics such as polymethylmethacrylate, nylon, polyethylene, polypropylene, and polycarbonate type materials; metals such as iron, gold, silver, nickel, tungsten, and copper; inorganic composites such as glass, ceramics, metallic oxides, cellulose and various modified celluloses.

EXAMPLE I

A microporous member of the preceding type was fabricated from three 47 mm polycarbonate filter sheets of the type presently sold by Nuclepore Corporation, Pleasanton, Calif. under the designation Stock No. 111101. These filter sheets are approximately 10 micron thick and are permeated with approximately 6×10^9 pores per square centimeter wherein the approximately circular cross section pores average about 0.015 micron in diameter. The foregoing polycarbonate filters were asymmetrically etched with 6.25 normal aqueous sodium hydroxide solution containing 0.05% (vol./vol. basis) of the surfactant sold under the trademark Dowfax 21 A, manufactured by Dow Chemical Company, Midland, Michigan, for a period of just five minutes on only one surface of the filter and at a temperature of 40°C . The membranes were then washed free of sodium hydroxide with water and dried. Three such asymmetrically etched filters were stacked, one on top of the other such that the taper of the holes pointed in the same direction. The stack of filters were then placed between the faces of two fritted glass discs manufactured by Corning Glass Works, Corning, N.Y. and listed in their Pyrex Labware Catalog Lab-I as No. 39535, Tube Immersion, With Fritted Disc, 60 M. The two Fritted Glass Discs with the oriented stack of filters between them were securely fastened together by means of three metal clamps. The surface of the Fritted Glass Discs which extended beyond the stack of filters and the edges of the stack of filters were sealed fluid tight with three coats of commercial epoxy type cement and allowed to cure thoroughly after each coat.

EXAMPLE II

A microporous member of the preceding type was fabricated from five 47 mm polycarbonate filter sheets of the type presently sold by Nuclepore Corporation, Pleasanton, Calif. under the designation Stock No. 111101. These filter sheets are approximately 10 micron thick and are permeated with approximately 6×10^9 pores per square centimeter wherein the approximately circular cross section pores average about 0.015 micron in diameter. The foregoing polycarbonate filters were asymmetrically etched with 6.25 normal aqueous sodium hydroxide solution containing 0.05% (vol./vol. basis) of the surfactant sold under the trade name Dow-

fax 21 A, manufactured by Dow Chemical Company, Midland, Mich. for a period of just five minutes on only one surface of the filter and at a temperature of 40° C. The etched filter was then wash free of sodium hydroxide with water and then dried. Five such asymmetrically etched filters were stacked, one on top of the other such that the tapers of the holes all pointed in the same direction. The stack of etched filters were then firmly clamped together to form the above microporous member by means of a clamping device. Examples of such clamping devices are those manufactured by Nuclepore Corporation and shown in their Catalog Lab-30 Pages 36 and 37 and identified as Plastic Filter Holder Stock No. 420400 and Stainless Steel In-Line Holder, 47 mm, Stock No. 421700.

It is envisioned that the microporous member of this invention could be fabricated from microscopic, generally pyramidal shaped particles by the two step process described below.

The requisite generally pyramidal shaped microscopic particles may be found in nature as is well known to those skilled in the arts of mineralogy and chemical microscopy and crystallography. These materials can be crystallized from a solution. Some of the substances which are known to crystallize in pyramidal shaped particles are tetraethyl ammonium chloride, silver chloride mono-hydrate, lithium potassium sulfate, potassium tetrathionate, sodium tellurium phosphate and pentarythritol and are listed in "Chemische Kristallographie" by P. Groth, published in Leipzig, Germany by Wilhelm Engelmann in 1905. Additionally, pyramidal shaped crystals are reported as zinc oxide in "Crystals", C. Bunn, Academic Press, New York, N.Y. 1964, on Page 95; and zincite (zinc oxide) in "Dana's Manual of Mineralogy", Revised by C. S. Hurlbut, Jr., 17th ed. Page 67, John Wiley, New York, N.Y. 1965.

For some applications it is anticipated that it will be described that the microporous member be fabricated out of other materials with quite different chemical and physical properties. Additionally, economics will play a key role in the choice of material and method of fabrication. Casting has been a time honored method for the production of a large number or uniformly shaped objects. We therefore anticipate that casting will be a significant method used for the fabrication of the requisite generally pyramidal shaped particles.

The two step process of fabrication of the microporous member noted above consists of:

a. The microscopic, generally pyramidal shaped particles are loosely packed in a layer, many particles thick, such that a substantial majority of the generally pyramidal particles have their apexes directed toward one surface of the layer and correspondingly a substantial majority of the bases of the generally pyramidal particles have their bases directed towards the second surface of the layer.

b. The oriented, packed, microscopic generally pyramidal shaped particles are affixed together by any of the standard methods for providing containment of the particles close to one-an-other and in the initial orientation. Such techniques include, but are not limited to: welding, pressing, clamping, sintering, gluing, sealing, and brazing.

The orientation of the microscopic generally pyramidal shaped particles described above in "a." can be accomplished by any of the various known techniques. These include but are not limited to: the application of electrical or magnetic fields such that the longer axis of

the generally pyramidal shaped particle will either line up parallel or perpendicular to the electrical or magnetic field depending upon whether the material used is diamagnetic, paramagnetic or ferromagnetic; the application of a force field; such as gravitational or centrifugal, while the particles are dispersed in a viscous fluid of a differing density from that of the pyramidal particles, whereby the generally pyramidal shaped particles will take up the same general orientation on moving through the viscous fluid such that in the packed layer of pyramidal particles the apexes will be generally pointing in one direction and the bases will be directed in the opposite direction.

I have found that when an appropriate microporous member, of the type described herein, is immersed in certain solutions, such as solution U, that a differential diffusional pressure, P_{dd} , develops in the solution U on the two opposite sides of the microporous member. When the differential diffusional pressure, P_{dd} , is not exactly balanced by the external pressure, P_o , the solution U flows through the microporous member at the rate J. The differential diffusional pressure, under zero net solution flow, P_{dd} , when $J=0$, and the net solution flow rate under zero differential external pressure, J_o , when $P_o=0$, are both useful for the characterization of the microporous member and the combination of a specific microporous member with a specific solution.

The average diameter of the solute particles, X, of the solution, U, employed in this invention, is at least 1.3 times as great as the average diameter of the solvent particles Y, of solution U. The average diameter of the solute particles X, of the solution U, employed in this invention is less than 500 times as great as the average diameter of the solvent particles Y, of solution U.

The concentration of the solute X in solution U, as used in this invention is greater than 0.01% and less than 90% on a weight/weight basis.

The solution U, used in this invention may be a true solution or a colloidal solution.

In general, a substantial majority of the pores and generally tapered voids permeating the microporous member will permit the diffusion of both the solvent particles, Y and the solute particles, X, making up the solution U, therethrough.

Any solution, provided it meets the above stated general restrictions and requirements may be used with the microporous member of this invention.

Specific examples of solvents and solutes, useful as constituents of the employed solution used in conjunction with the microporous member of this invention are enumerated below. This group is only illustrative and is in no way restrictive.

Solvents.

Water
Alcohols such as methanol and ethanol
Hydrocarbons such as hexane and benzene
Ammonia in the liquid state

Solutes.

Inorganic salts such as sodium chloride sodium sulfate.
Organic salts such as sodium benzoate and sodium dioleoyl sulfate.
Organic such as butanol, ethylene glycol, polyethylene, sucrose, and inulin.

Sea water is a particularly plentiful solution which can be used with the microporous member of the present invention.

I have found that when an appropriate microporous member, of the type described herein, is placed in a gaseous pressure gradient, that the effusional resistance of the said microporous member to gas flow is asymmetric.

Some characteristics of the interaction of the microporous member of this invention and a gas, G, may be set forth by a series of equations as set out below wherein: R_A = the absolute effusional resistance of the microporous member to a specified gas, G, in the first direction from side "i" of the microporous member to side "ii" of the microporous member.

T = the absolute temperature, °K, of the gas adjacent to the microporous member.

P_i = the pressure of the gas on side "i" of the microporous member.

d = thickness of the microporous member.

A = the area of the microporous member.

Q = the net gas flow rate through the area A of the microporous member.

R_B = the absolute effusional resistance of the microporous member to the specified gas, G, in the second direction from side "iii" of the microporous member to side "iv" of the microporous member.

P_{ii} = the pressure of the gas on side "iii" of the microporous member.

When the gas pressure is set so that P_i is the operating pressure on side "i" at T °K, and at the same time P_{ii} is held near zero Torr so that P_i is much greater than P_{ii} , R_A is defined by Equation (2):

$$R_A = AP_i / Q_d \quad (2)$$

and correspondingly when the gas pressure is set so that P_{ii} is the operating pressure on side "iii" at T °K, and at the same time P_i is held near zero Torr so that P_{ii} is much greater than P_i , R_B is defined by Equation (3):

$$R_B = AP_{ii} / Q_d \quad (3)$$

When, for a particular microporous member with a particular gas and at a temperature, T °K, if R_A and R_B , the absolute effusional resistance of the given microporous member in the two opposite directions, as calculated from Equations (2) and (3) respectively are not equal under conditions where P_i and P_{ii} in Equations (2) and (3) respectively are equal, then the microporous member's absolute effusional resistance is anisotropic for those specific operating conditions.

The microporous member's mean absolute effusional resistance coefficient, ϵ , is defined by Equation (4):

$$\epsilon = \frac{2(R_A - R_B)}{R_A + R_B} \quad \text{Equation (4)}$$

and ϵ is a measure of the microporous member's anisotropy. For a given single microporous member and a given gas under specified temperature and pressure, the mean absolute effusional resistance coefficient, ϵ , must be greater than 10^{-4} and less than 2.0, and may have intermediate values such as 0.1.

A wide variety of gases and mixtures of gases, can be used in conjunction with the microporous member of the present invention, such as but not limited to: air, water in the vapor state, hydrogen, helium, argon, ammonia, sulfur dioxide, hydrocarbons such as methane, perhalogenated hydrocarbons such as tetrafluoromethane and octafluorocyclobutane, partially halogenated hydrocarbons such as dichloromethane, nitrogen, oxygen, and flourine.

The temperature and pressure of the gas used in conjunction with the microporous member of the present

invention cover a very wide range limited only by the chemical and physical stability of both the gas and the particular microporous member and that value of the absolute effusional resistance coefficient, ϵ , for the system in question, is greater than 10^{-4} and less than 2.0. With these caveats and restrictions, the member is operational at any pressure or temperature which does not degrade or destroy the member.

With rod shaped molecules and rod shaped solute particles, the use of the members of the present invention are especially effective. This is believed to occur because the tapered part of the opening tends to orient the molecules or particles and permit their passage through the member in the direction from the wide opening side to the narrow opening side.

The present embodiments of this invention are thus to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims therefore are intended to be embraced therein.

I claim:

1. A microporous membrane of a relatively fluid impermeable material having first and second surfaces, permeated by numerous asymmetric pores comprising a series of sequentially directly interconnected generally tapered voids, wherein substantially all of the generally tapered voids are oriented such that the apex of said generally tapered voids are directed toward the first surface of the microporous membrane and substantially all of the bases of the generally tapered voids are directed toward the second surface of the microporous membrane, and wherein a fluid, upon passing completely through the microporous membrane will pass through at least three and generally less than 10,000,000 sequentially connected generally tapered voids, and wherein the microporous membrane is greater than about 0.001 micron in thickness and less than about 100 centimeters in thickness, and wherein the average distance across the base of each of the generally tapered voids is greater than about 0.001 micron and less than about 100 micron and wherein the average angle at the apex of each of the generally tapered voids is greater than about 10° and less than about 160° , and wherein the average distance across the ports interconnecting the generally tapered voids is greater than about 0.0002 micron and less than about 100 microns, and wherein the pores interconnecting the voids are fluid impervious so that fluid can only flow through the voids and interconnecting ports and wherein there are on the average at least two and less than 16 ports interconnecting each of the generally tapered voids, and wherein the average number of asymmetric pores passing through the microporous membrane is greater than about 10 per square centimeter.

2. The microporous membrane of claim 1 wherein the average number of asymmetric pores passing through the microporous membrane is less than about 10^{14} per square centimeter.

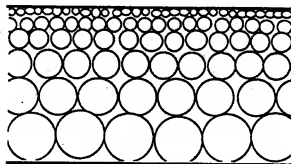
3. The microporous membrane of claim 1 wherein said membrane is surrounded by a gas.

4. The microporous membrane of claim 1 wherein said membrane is surrounded by a solution wherein the average diameter of the solute particles of said solution is at least 1.3 times as great as the average diameter of the solvent particles, and wherein the average diameter of the solute particles is less than 500 times as great as the average diameter of the solvent particles.

* * * * *



US005236588A

United States Patent [19]**Zhang et al.**[11] **Patent Number:** **5,236,588**[45] **Date of Patent:** **Aug. 17, 1993****[54] ASYMMETRIC POLYMER MEMBRANE
AND PREPARATION THEREOF****[75] Inventors:** Husheng Zhang, Sakura; Takamori
Anazawa, Sakura; Kazunari Sakai,
Chiba, all of Japan**[73] Assignee:** Dainippon Ink and Chemicals, Inc.,
Itabashi, Japan**[21] Appl. No.:** 777,706**[22] Filed:** Oct. 18, 1991**[30] Foreign Application Priority Data**
Oct. 18, 1990 [JP] Japan 2-277912**[51] Int. Cl.:** B01D 67/00**[52] U.S. Cl.:** 210/500.35; 264/41;
264/45.1; 264/DIG. 48; 264/DIG. 62**[58] Field of Search:** 210/500.35, 500.27,
210/500.21, 500.34; 264/41, 45.1, DIG. 48,
DIG. 62**[56] References Cited****U.S. PATENT DOCUMENTS**3,615,024 10/1971 Michaels .
3,926,864 12/1975 Hodgdon, Jr. .
4,659,470 4/1987 Canaba et al. .
4,775,474 10/1988 Chau et al. 210/500.54**FOREIGN PATENT DOCUMENTS**2301552 7/1973 Fed. Rep. of Germany .
2301553 7/1973 Fed. Rep. of Germany .
22116306 7/1972 France .
2406469 5/1979 France .
2124973 2/1984 United Kingdom .**OTHER PUBLICATIONS**Gerald B. Tanny, Ph. D., "The High Surface Area--
Low Driving Force Alternative in Gas Separation",
Proc. 4th Ann. Membrane Technology Planning Con-
ference, pp. 231-243 (1986).
Derwent Abstract, No. 88-1124357, Section Ch, week
8818 of JP 63-069845, Mar. 29, 1988, (Dainippon Print-
ing Co. Ltd.).**Primary Examiner**—Frank Sever
Attorney, Agent, or Firm—Armstrong, Westernman,
Hattori, McLeland & Naughton**[57]****ABSTRACT**An asymmetric polymer membrane is disclosed charac-
terized by being formed by irradiating a monomer and/
or an oligomer polymerizable with an energy ray and
having a pore diameter distribution in the thickness
direction of the membrane, a ratio of a permeability flux
of oxygen to nitrogen of 0.9-1.1, and communicating
pores.**8 Claims, 3 Drawing Sheets**

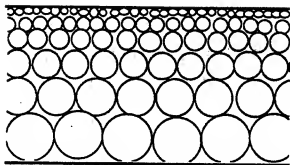


FIG. 1

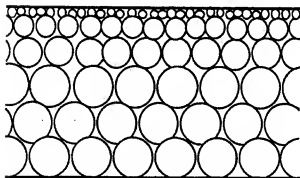


FIG. 2

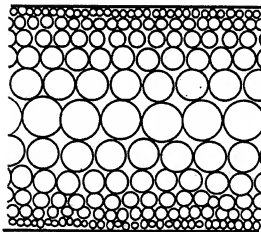


FIG. 3

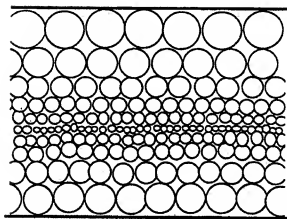


FIG. 4

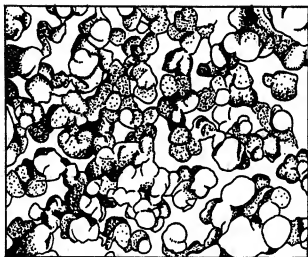


FIG. 5

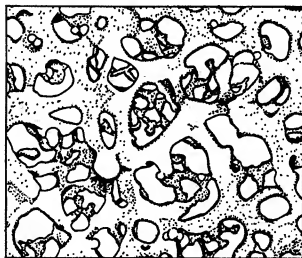


FIG. 6

ASYMMETRIC POLYMER MEMBRANE AND
PREPARATION THEREOF

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a porous membrane such as an ultrafiltration membrane, a reverse osmosis membrane, a microfiltration membrane, etc., used for the purpose of filtration and separation of proteins, colloids, bacteria, viruses, salts, etc., in various separation processes in the food industry, pharmaceutical industry, and electronics industry, and in waste water treatment, artificial organs, purification of fresh water from sea water, etc., and in addition relates to the preparation of such a membrane.

2. Prior Art

As a method for preparing porous membranes, there has been a so-called wet process in which a polymer is dissolved in a solvent and a transformation procedure from a sol to a gel was utilized, as well as a method in which both a polymer compound and a material which were extractable by a nonsolvent were dissolved in a solvent suitable for both compounds, and after a film was made by evaporating the solvent, the film was extracted with the non-solvent.

However, in these methods, not only were there problems in that the production speed was slow, but also it was necessary to prepare a polymer solution, and it was impossible to obtain a porous membrane having excellent strength, heat resistance and chemical resistance.

In order to solve these problems, a membrane with a cross-linked structure was prepared. As a method for making this possible, in Japanese Patent Publications No. 34,329/1981 and No. 65,220/1988, a method was described for preparation of a porous membrane with a cross-linked structure in which a polymerizable monomer and/or oligomer were polymerized in the presence of a non-solvent which acted as a solvent for the monomer and/or oligomer, and did not swell a polymer made of these monomers. Furthermore, in Japanese Laid Open Patent No. 107,062/1974, an asymmetric membrane was described characterized by the membrane consisting of a covalently cross-linked vinyl polymer.

However, even though a porous membrane with excellent strength, heat resistance, and chemical resistance could be obtained with high production speed by the method of Japanese Patent Publications No. 34,329/1981 and No. 65,220/1988, since a porous membrane with a uniform pore diameter distribution in the cross-sectional direction of the membrane was obtained, in order to obtain a porous membrane with an arbitrary filtering separability, it was necessary to select membrane forming conditions in very narrow ranges. In addition, when filtering separation was performed by using the porous membrane, there were problems in that the permeation speed of the filtrate was extremely low and fouling of the membrane occurred easily. Furthermore, the method of Japanese Patent Publication No. 65,220/1987 was restricted to a method for preparation of a finely porous membrane with a fine pore dimension of 0.02-15 micrometers and without the capability of molecular weight cut-off.

In addition, in the Proceedings of the Fourth Annual Membrane Technology/Planning Conference 231 (1986), there was given a description of an asymmetric polymer membrane obtained by irradiating a homo-

neous polymerizable solution in which a monomer and/or an oligomer were polymerizable by irradiation by an energy ray, and a non-solvent which acted as a solvent for the monomer and/or the oligomer and which did not swell or dissolve a polymer produced of the monomer and/or oligomer cured by an energy ray. However, in this reference, only a description of a gas separation membrane with a ratio of permeation of oxygen to nitrogen of 2.9-4.2 was given; that is, one having no pores which communicate with one another which could let a liquid pass through, and no description was given of a practical method for preparation thereof.

In addition, in the method of Japanese Laid Open Patent Publication No. 107,062/1974, as this asymmetric membrane was prepared by exploiting the freezing of a solvent (hereinbelow described as a "freezing method"), the thickness of a layer with a smaller pore diameter than that of the other parts in the thickness direction of the membrane (hereinbelow described as a dense layer) was 50 micrometers or greater, and this resulted in the filtering rate being very low; and the pore diameter of a layer with a larger pore diameter than that of either part in the thickness direction of the membrane, (hereinbelow described as a "porous supporting layer") and resulted in a membrane with insufficient membrane strength. This is not practical.

SUMMARY OF THE INVENTION

It is therefore a purpose of the present invention to provide an asymmetric polymer membrane which can be produced at a high speed, and with which an arbitrary filtering separability is easily obtained as the membrane has pore diameter distribution in the thickness direction of the membrane, and has pores which communicate with each other which can allow a liquid to pass through, which has not only extremely high or good filtering speed but also high molecular weight cut-off ability, which resists fouling and which exhibits excellent strength, heat resistance, and chemical resistance due to a cross-linked structure. It is another purpose to offer a method for preparation thereof.

The present inventors have performed extensive research to solve the above-described problems, and the present invention is the results of their efforts.

That is, the present invention offers an asymmetric polymer membrane formed by irradiating a monomer and/or an oligomer which are polymerizable by irradiation with an energy ray; the membrane having a pore diameter distribution in the depth of the membrane and a ratio of permeation flux of oxygen/nitrogen (hereinbelow abbreviated as a "separation factor") of 0.9-1.1 and with pores which communicate with each other; and a method for preparation thereof. The present invention furthermore offers an asymmetric polymer membrane formed by irradiating a monomer and/or an oligomer which are polymerizable by irradiation with energetic radiation. The asymmetric polymer membrane has an asymmetric pore diameter distribution in the depth of the membrane, and in which the thickness of its dense layer is 5 micrometers or less, the thickness of its porous supporting layer is 0.1-20 micrometers. When the diameter of the pores in the dense layer is 0.0005-0.015 micrometer, the membrane has a molecular weight cut-off ability, when the pore diameter of the dense layer is 0.02-20 micrometers, the membrane does

not have a molecular weight cut-off ability. The present invention offers a method for preparation thereof.

A monomer and/or an oligomer of the present invention can be used as a homogeneous polymerizable solution by mixing with a non-solvent which acts as a solvent for the monomer and/or the oligomer, but does not swell or dissolve a polymer formed of the monomer and/or oligomer. In addition, it is possible to incorporate a second solvent which swells or dissolves a polymer formed of the monomer and/or oligomer in the homogeneous polymerizable solution.

An asymmetric polymer membrane with a pore diameter distribution in the thickness direction of the membrane can be obtained by polymerizing the homogeneous polymerizable solution by irradiating it with energetic radiation after a part of the non-solvent and/or the solvent is evaporated from the homogeneous polymerizable solution.

In addition, an asymmetric polymer membrane with a pore diameter distribution in the cross-sectional direction of the thickness of the membrane can be obtained by polymerizing the homogeneous polymerizable solution by irradiating with energetic radiation under a temperature gradient in the thickness direction of the membrane.

As an asymmetric polymer membrane of the present invention has a pore diameter distribution in the thickness direction of the membrane and communicating holes capable of allowing a liquid to pass through, an arbitrary filtering separator can be easily obtained in which the filtering speed is high and in which fouling is unlikely to occur. In addition, as it has a cross-linked structure, strength, heat resistance, and the chemical resistance of the membrane are excellent. Furthermore, there exists an advantage of high production speed.

In addition, in comparison with conventional wet methods and other methods for preparing asymmetric membranes, the method of preparation of the present invention is such that chemical modifications of the membrane are easy to perform; a cross-linked structure can be introduced in the membrane; the production speed is high as the phase separation is substantially and spontaneously completed; use of a high boiling polar solvent, such as dimethylformamide, the waste treatment of which is difficult, can be avoided; and, in comparison to such methods for introducing a cross-linked structure by cross-linking the film of the thermoplastic polymer by radiation, etc., has such features that the production speed is high; an apparatus on a large scale is unnecessary; the range of selection of polymers is wide; and design of the cross-linking density and cross-linking structure are easy to produce.

As monomers used for the present invention, monofunctional monomers such as ethyl (meth)acrylate, hydroxyethyl (meth)acrylate, n-butyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, phenyl (meth)acrylate, phenylcellosolve (meth)acrylate, n-vinylpyrrolidone, isobornyl (meth)acrylate, dicyclopentenyl (meth)acrylate and dicyclopentenyl-oxethyl (meth)acrylate, difunctional monomers such as diethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,6-hexane diol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 2,2-bis(4-(meth)acryloyloxyphenyl)propane and 2,2-bis(4-(meth)acryloyloxypropyl)propane, trifunctional monomers such as trimethylolpropane tri(meth)acrylate and trimethylolmethane tri(meth)acrylate, tetrafunctional monomer such as pentaeryth-

ritol tetra(meth)acrylate, and hexafunctional monomers, such as dipentaerythritol hexa(meth)acrylate, can be cited.

As oligomers used in the present invention, for example, those which are polymerizable by irradiation by energetic radiation and have a weight average molecular weight of 500-50,000, can be cited; and in practice, an acrylate or methacrylate of an epoxy resin, an acrylate or methacrylate of a polyester resin, an acrylate or methacrylate of a polyether resin, an acrylate or methacrylate of a polybutadiene resin and a polyurethane resin having acrylic groups or methacrylic groups on its molecular terminals, can be cited.

Selection of the monomer and/or the oligomer may be determined by the necessary heat resistance, strength, molecular weight cut-off ability, etc., of the polymer membrane. For example, to obtain a polymer membrane with excellent heat resistance, polyfunctional monomers and/or oligomers are selected. In contrast, when no heat resistance is required, only monofunctional monomers and/or oligomers may be selected. Furthermore, to produce such a polymer membrane which can filter substances having relatively low molecular weights, it is preferable that polyfunctional monomers and/or oligomers be selected, and that the molecular weight between cross-links be small. In contrast, to produce a polymer membrane which can filter substances with relatively large molecular weights, it is preferable that monomers and/or oligomers with low functionalities and large molecular weights be selected to make the molecular weight between cross-links large.

As the non-solvent used in the present invention, any solvent that can homogeneously dissolve monomers and/or oligomers used in the present invention, and which does not swell or dissolve the polymers formed of these monomers and/or oligomers, can be used. For example, when a polyurethane resin with acrylic groups on the ends of the molecule is used as an oligomer, alkyl esters such as methyl caprate, and dialkyl ketones such as diisobutyl ketone, etc., are preferably used as the non-solvent. Solubility and boiling point of the non-solvent can be suitably selected depending on the kind of the monomer and/or the oligomer, the necessary molecular weight cut-off ability, and the necessary degree of structural asymmetry.

When a method of preparation is used in which a part of the non-solvent is evaporated, there are correlations between the evaporation of the non-solvent and the degree of the asymmetry of the structure. The degree of the asymmetry of the structure correlates with the molecular weight cut-off ability and the amount of permeation of a filtrate. Therefore, selection of the boiling point of the non-solvent is possibly one of the important factors determining the filtering characteristics of the obtained polymer membrane. One example related to the selection of boiling point of the non-solvent is that when a part of the non-solvent is evaporated at or below room temperature, and when the speed of the air flow blown on a polymerizable solution for evaporating a part of the solvent is low, or when the non-solvent should be evaporated in an extremely short time, a substance with a boiling point of 80 degrees C. or lower can be used as the non-solvent. In addition, when heated air is blown on the polymerizable solution, or when the non-solvent should be evaporated over a certain prolonged period, a substance with a boiling point of 60 degrees C. or higher can be used as the non-solvent. In

addition, the non-solvent may be a mixture of two or more chemicals.

As the solvent used in the present invention, any solvent that can homogeneously dissolve monomers and/or oligomers, and can swell or dissolve polymers formed of these monomers and/or oligomers, may be used. For example, when a polyurethane resin with acrylic groups on its molecular ends is used as the oligomer, acetone, methyl ethyl ketone, ethyl acetate, dimethylformamide, *n*-methyl-pyrrolidone, etc., can be suitably used as the solvent. Solubility and boiling point of the solvent can be appropriately selected, depending on the kinds of the monomers and/or the oligomers, the necessary molecular weight cut-off ability, and the necessary degree of the asymmetry in the structure.

When a solvent is incorporated in a polymerizable solution, the range of solubility control is widened, and accordingly, the range of selection of non-solvents, polymerizable monomers and oligomers, and additives can be widened, and it thus becomes easier to improve membrane characteristics and to prepare a membrane in accordance with the desired use and purpose. In addition, it becomes easier to form a dense layer at an arbitrary position such as on the gas phase side, on the supporting body side or on the inner part of the membrane, by controlling the combination of boiling points of the non-solvent and the solvent.

As in the case of the boiling point of the non-solvent, selection of the boiling point of the solvent is also possibly one of the important factors determining filtering characteristics of the obtained polymer membrane, and it is necessary to select it based on the same considerations as in the case of the non-solvent. In addition, in many cases, there exists a correlation between the solubility of the solvent and the molecular weight cut-off ability of the obtained polymer membrane. To give one example, in order to obtain a polymer membrane which can filter substances with relatively small molecular weights, a solvent with a high solubility can be used. In addition, to obtain a polymer membrane which can filter substances with relatively large molecular weights, a solvent with a low solubility may be used.

The weight ratio of a non-solvent and solvent to the monomer and/or an oligomer is preferably in the range of 0.1-4.0 per monomer and/or oligomer. If it is 0.1 or less, a sufficient amount of permeation is not obtained, and if it is 4.0 or larger, the strength of the membrane will be insufficient.

As energetic rays used in the present invention, electron beams, gamma rays, X-rays, UV rays, visible rays, etc., may be used. Among these rays, it is desirable to use UV rays because of the simplicity of the apparatus therefor the manipulation thereof. The strength of the irradiating UV rays is preferably 10-500 mW/cm², and the irradiation time is usually about 0.1-100 seconds. When UV rays and visible rays are used as the energetic rays, it is possible to incorporate photopolymerization initiator in the polymerizable solution to accelerate the rate of polymerization. In addition, it is possible to further accelerate the polymerization by performing the irradiation by UV rays under an inert gas. An electron beam is another preferred energy ray which may be used for the present invention. When an electron beam is used, since there is no absorption of UV rays by the solvent, the non-solvent, and the other additives, the range of selection of these substances is widened and the rate of membrane formation is also improved.

As a UV polymerization initiator which can be mixed with a polymerizable solution of the present invention, acetophenones such as *p*-tert-butyltrichloroacetophenone, 2,2-diethoxyacetophenone and 2-hydroxy-2-methyl-1-phenylpropane-1-one, ketones such as benzophenone, 4,4-bisdimethylaminobenzophenone, 2-chlorothioxantone, 2-methylthioxantone, 2-ethylthioxantone and 2-isopropylthioxantone, benzoin ethers such as benzoin, benzoin methyl ether, benzoin isopropyl ether and benzoin isobutyl ether, benzyl ketals such as benzyl dimethyl ketal and hydroxycyclohexyl phenyl ketone, can be cited.

As a method of transforming a polymerizable solution into a thin membrane in the present invention, a method of coating a supporting body with a polymerizable solution by means of a roll coating method, a doctor blade method, a spin coating method, a spray method, etc., may be used. As the supporting body, a metal, a ceramic, a glass, a plastic, a fabric, a non-woven fabric, a paper, etc., can be used. When a belt-like material is used as the supporting body, a continuous thin film can be formed. The membrane can eventually be peeled off of the supporting body; when the supporting body is porous, the product can be used integrated as it is. In addition, it is possible to use a method in which a thin membrane is formed without using a supporting body.

In the specification of the present invention, the phrase "having a pore diameter distribution in the depth of the membrane" means that a large number of pores of various diameters which vary continuously or discontinuously in the depth of the membrane. An example of the pore diameter distribution, in the case in which the pore diameters increase or decrease continuously from one surface of the membrane to the other surface thereof, is illustrated in FIG. 1. An example of the pore diameter distribution, in the case in which the pore diameters increase or decrease discontinuously from one surface of the membrane to the other surface thereof, is illustrated in FIG. 2. An example of the pore diameter distribution, in the case in which layers of pores having relatively small diameters exist near both surfaces of the membrane, and the pore diameters increase continuously or discontinuously from the surfaces of the membrane to the middle thereof, is illustrated in FIG. 3. An example of the pore diameter distribution, in the case in which there is a layer of pores having the smaller relative diameters at the middle of the membrane, and in which the pore diameters increase continuously or discontinuously from both sides of the middle pore layer to the surfaces of the membrane, is illustrated in FIG. 4.

The phrase "pores which communicate with one another" in the specification means that the pores are connected to permit the passage of liquid from one surface of the membrane to the other surface. When the liquid being filtered is water, a hydrophobic membrane with pores which communicate with one another will not permit water to pass through unless great pressure is applied to one side of the membrane.

However, such a membrane will permit the passage of water if the membrane is first dipped in an alcohol or an aqueous solution of a surfactant.

The shape of the pores which communicate with one another in the asymmetric polymer membrane according to the present invention is not limited. For example, the shape of the pores which communicate with one another may comprise gaps between spherical domains

of polymers in contact with one another; this situation is illustrated in FIG. 5. Another example, in which the polymers form a sponge-like structure, is illustrated in FIG. 6.

As asymmetric polymer membrane of the present invention is a membrane that consists of a dense layer and a porous supporting layer.

It is desirable that the thickness of the dense layer be 5 micrometers or less. If the thickness is 5 micrometers or greater, the filtration speed is extremely low, and this is not practical. In addition, there is a practically attainable lower limit to the thickness of the membrane, but as there is no problem caused by the thinness of the membrane itself, there is no theoretical lower limit to the thickness of the membrane.

In addition, it is preferable that in the porous supporting layer, the pore diameter of the pores be 0.1-20 micrometers. If the pore diameter is 0.1 micrometer or less, the filtration speed is extremely low, and this is not practical. In addition, if the pore diameter is 20 micrometers or greater, the strength of the membrane is extremely low, and this is again not practical.

As described above, the dense layer and the porous supporting layer may be located on one surface of a membrane or on both surfaces thereof. Therefore, such a membrane having a dense layer inside and porous supporting layers on both surfaces, is to be included in the membranes of the present invention.

The membrane of the present invention has pores which communicate with one another, has pore diameters of 0.0005-20 μm in the dense layer, and is capable of allowing a liquid to pass through. When the pore diameters of the holes of the dense layer of the membrane are 0.0005-0.015 μm , the membrane has a molecular weight cut-off ability and can separate polymer substances, low molecular weight substances, or ions dissolved in a solvent, from the solvent. Therefore, in this case, the membrane is suitable as an ultrafiltration membrane, a reverse osmosis membrane, etc.

The assessment as to whether the pore diameter of holes in the dense layer is not to be less than 0.0005 μm can be performed by noting whether the following separation factor of oxygen and nitrogen is in the range of 0.9-1.1. The assessment as to whether the pore diameters of holes in the dense layer are not greater than 0.015 μm or not, can be performed by a filtration test using a substance with an apparent diameter, such as a protein or the like. When the pore diameters of holes of the dense layer of the membrane are 0.02-20 μm , the membrane does not have a molecular weight cut-off ability and allows polymer substances, low molecular weight substances, and ions to pass through. Therefore, in this case, the membrane is suitable as a microfiltration membrane, etc. The assessment as to whether the pore diameters of holes in the dense layer are not less than 0.02 μm can be performed by a filtration test using a substance with an apparent diameter, such as a microbe. The assessment as to whether the pore diameter is not greater than 20 μm can be performed by electron microscopic observations.

In addition, as the membrane of the present invention has a separation factor of 0.9 to 1.1 and the permeation rates of oxygen and nitrogen are at the same level, the membrane has no gas separation ability. If the pore diameters of the holes in the dense layer of the membrane are less than 0.0005 μm , a gas may pass through the membrane according to the dissolution-diffusion principle. The separation factor thereof depends on the

material of the membrane; however, it is generally not less than 2. When the pore diameters of the pores which communicate with one another in the dense layer are not less than 0.0005 μm , a gas moves through the membrane according to the Knudsen flow or the Poiseuille flow. The separation factor thereof is 0.9 to 1.1 ("An Outline of Membrane Treatment Technique", Vol. 1, 1991, page 24, supervised by Masayuki Nakagaki, Fuji Techno System).

Furthermore, the ratio of the pore diameter in the dense layer to the mean pore diameter of the entire membrane is in a range of 10^{-6} to 10^{-1} in the membrane of the present invention.

In addition, the density of the pores in the membrane of the present invention, that is, the void content, is preferably 10-70%. If the void content is 10% or less, the filtration speed is extremely low, and this is not practical. In addition, if it exceeds 70%, the strength of the membrane is extremely low, and this is again not practical.

The present inventors found that there were various methods for polymerizing a polymerizable solution into a porous thin membrane having an pore diameter distribution in the thickness direction of the membrane by irradiation with an energy ray.

A method can be cited in which after a polymerizable solution is formed into a thin membrane and a part of a non-solvent is evaporated, the thin membrane is irradiated with an energy ray; another method can be cited in which a solvent is incorporated in a polymerizable solution and after a part of this solvent and/or a non-solvent is evaporated, this thin membrane is irradiated with an energy ray; and yet another method can be cited in which after a polymerizable solution is formed into a thin membrane, this membrane is irradiated with an energy ray while a temperature gradient is provided in the thickness direction of the membrane.

In order to evaporate a part of a solvent or a non-solvent, methods may be chosen such as a method in which air, nitrogen, or an inert gas is blown on a polymerizable solution of a thin membrane-like condition; a method in which drying is performed for a specified time without blowing a gas over the membrane; and a method in which infrared rays are used. In order to evaporate selectively a portion of the solvent or the non-solvent, the evaporation is performed by selecting substances, each having a different boiling point.

When no temperature gradient exists and a non-solvent, or both the non-solvent and the solvent, is nonvolatile, that is, under a condition in which the non-solvent or the solvent is not evaporated, an asymmetric structure is not formed. In addition, under a condition in which the non-solvent or the solvent is completely evaporated without any trace, only a non-porous homogeneous membrane or a symmetric porous membrane is obtained by radiation curing. An asymmetric membrane consisting of a dense layer and a porous supporting layer cannot be obtained until a portion of a solvent or a non-solvent is evaporated.

In the present method, it is possible to easily introduce a cross-linked structure on a membrane (in comparison with other methods for preparing an asymmetric membrane such as wet methods and others) and to realize an extremely high production speed by evaporation in an extremely short time and to produce phase separation substantially and spontaneously. In addition, in comparison with a freezing method, a high flux based on a thin dense layer, a high pressure-resistant strength

resulting from a not-too-large pore diameter in a porous supporting layer, and a high production speed, can be realized.

As a method for providing a temperature gradient, a method in which a temperature of a supporting body and an atmospheric temperature or a gas flow temperature are made to differ from each other, and a method by means of infrared heating, may be used.

A method of preparation in which an asymmetric structure is introduced by irradiating with energetic radiation under a condition in which a temperature gradient is provided to a polymerizable solution has features exhibiting superior production speed and reproducibility over a method in which irradiation with energetic radiation is performed after a part of a solvent or a non-solvent is evaporated.

The reason why and the mechanism by which a porous thin membrane with a pore diameter distribution in the thickness direction of the membrane is obtained in the present invention has not yet been solved; however, it is hypothesized that the reason is that an nonhomogeneous phase separation is produced in the thickness direction of the membrane by irradiating with antineutrino radiation under a condition in which a concentration distribution of a monomer and/or an oligomer or a distribution of a concentration ratio of the non-solvent to the solvent is formed by evaporating a part of the monomer and/or the oligomer and under a condition in which a temperature gradient is formed in the thickness direction of the membrane.

In addition, it is estimated that when a thin membrane of a polymerizable solution is formed on a supporting body, evaporation of a non-solvent or a solvent from only one face of the polymerizable solution and difference in compatibility between each ingredient of the polymerizable solution and the supporting body contribute to generate the asymmetric pore diameter distribution.

It is necessary that after polymerization is finished by irradiating with an energy ray, a non-solvent and a solvent are removed by means of evaporation and/or washing. For the washing, a washing agent which can dissolve thoroughly the non-solvent, the solvent, unreacted monomers and/or oligomers and a UV polymerization initiator and does not swell or dissolve a polymer can be used and a cleaning agent with a low boiling point is preferable. In addition, the cleaning can be performed in a plurality of processes using a plurality of cleaning agents.

As an asymmetric polymer membrane of the present invention exhibits high filtration rate, excellent strength, heat resistance, and chemical resistance, it is possible to apply it effectively to an ultrafiltration membrane, a reverse osmosis membrane, a precision filtration membrane, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-4 are enlarged sectional views showing a membrane structure having a pore diameter distribution in the thickness direction of the membrane according to the invention. The inside of the circles in these FIGURES represent hole portions in the membrane.

FIGS. 5 and 6 are drawings taken from electron micrographs showing Examples of the shape of pores which communicate with one another according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

Hereinbelow, the present invention will be explained in detail, but the range of the present invention is not restricted to these examples. "Parts" in the examples refer to parts by weight.

EXAMPLE 1

Preparation of a polymerizable solution

A polymerizable solution 1 was obtained by mixing 100 parts urethane acrylate oligomer with a number average molecular weight of 1,000 and three acrylic groups on average per molecule, 4 parts UV polymerization initiator Irgacure-651 (manufactured by Ciba-Geigy Co., Ltd.) and 70 parts diisobutyl ketone (a non-solvent).

Preparation of an asymmetric polymer membrane

A glass plate was coated with the polymerizable solution 1 by means of a film applicator so as to obtain a thickness of 200 micrometers. After a part of the non-solvent was evaporated by keeping the glass plate under a nitrogen flow for 2 minutes, the coating was irradiated with a UV ray having a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds by means of a metal halide lamp. It was observed that the coating film which was transparent before irradiation became opaque and white after irradiation. The obtained opaque white membrane was peeled off from the glass plate and the non-solvent, unreacted monomer and oligomer, and the UV polymerization initiator were washed out by immersion in petroleum ether for 30 minutes. By thoroughly drying the membrane after cleaning, an asymmetric polymer membrane 1 with a luster on the glass plate side and no luster on the side brought into contact with the nitrogen flow was obtained.

By observing the polymer membrane 1 by means of an electron microscope, it was found that the pore diameter on the glass plate side was about 0.01 micrometer, while the pore diameter on the side brought into contact with the nitrogen flow was about 2 micrometers. In addition, by observing a cross-section, it was found that a part with smaller pore diameters only existed in an extremely thin layer on the glass plate side, and the thickness was 1 micrometer or less. The separation factor of oxygen/nitrogen was 0.980.

Evaluation of filtration characteristics

A filtration experiment of a 0.3% aqueous solution of polyethylene glycol with a molecular weight of 50,000 was performed by using an ultrafiltration apparatus SM-165-26 manufactured by Zaltorius Co., Ltd. Flux (transmittance) with a polyethylene glycol aqueous solution; rejection results of polyethylene glycol at a filtration temperature of 25 degrees C. and under a filtration pressure of 3 kg/cm² are shown in Table 1. The same evaluations were performed in the following Examples and Comparative Examples.

EXAMPLE 2

Preparation of a polymerizable solution

A polymerizable solution 2 was obtained by mixing 60 parts urethane acrylate oligomer with a number average molecular weight of 3,000 and three acrylic groups on average per molecule, 20 parts 1,6-hexane

diol diacrylate, 4 parts Irgacure-651 (a UV polymerization initiator manufactured by Ciba-Geigy Co., Ltd.), 20 parts diisobutyl ketone (a non-solvent), and 70 parts methyl caprate (a non-solvent).

Preparation of an asymmetric polymer membrane

By performing the same procedures as in Example 1, an asymmetric polymer membrane 2 with a luster on the glass plate side and no luster on the side brought into contact with the nitrogen flow was obtained. Results of observations by means of an electron microscope were the same as those in Example 1. In addition, the separation factor of oxygen/nitrogen was 0.935.

EXAMPLE 3

Preparation of a polymerizable solution

A polymerizable solution 3 was obtained by mixing 50 parts urethane acrylate oligomer with a number average molecular weight of 1,000 and two acrylic groups on average per molecule, 30 parts acrylate of an epoxy resin with an epoxy equivalent of 190, 20 parts phenylcellosolve acrylate, 4 parts Irgacure-184 (a UV polymerization initiator manufactured by Ciba-Geigy Co., Ltd.), 70 parts methyl caprate (a non-solvent), and 30 parts acetone (a solvent).

Preparation of an asymmetric polymer membrane

A glass plate was coated with the polymerizable solution 3 by means of a film applicator so as to obtain a thickness of 200 micrometers. After a part of the solvent was evaporated by keeping the glass plate under a nitrogen flow for 30 seconds, the coating was irradiated with a UV ray having a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds from a metal halide lamp. It was observed that the coating film which was transparent before irradiation became opaque and white after irradiation. The obtained opaque white membrane was peeled off from the glass plate and the non-solvent, solvent, unreacted monomer and oligomer, and the UV polymerization initiator were washed out by immersion in petroleum ether for 30 minutes. By thoroughly drying the membrane under a vacuum after cleaning, an asymmetric polymer membrane 3 with a luster on the glass plate side and no luster on the side brought into contact with the nitrogen flow was obtained.

Results of observations by means of an electron microscope were the same as in Example 1. In addition, the separation factor of oxygen/nitrogen was 0.936.

EXAMPLE 4

Preparation of a polymerizable solution

A polymerizable solution 4 was obtained by mixing 60 parts urethane acrylate oligomer with a number average molecular weight of 3,000 and two acrylic groups on average per molecule, 20 parts trimethylolpropane triacrylate, 20 parts neopentyl glycol diacrylate, 4 parts Irgacure-651 (a UV polymerization initiator manufactured by Ciba-Geigy Co., Ltd.), 70 parts methyl laurate (a non-solvent), and 30 parts methyl isobutyl ketone (a solvent).

Preparation of an asymmetric polymer membrane

A polymer membrane 4 with a luster on the side brought into contact with the nitrogen flow and no luster on the glass plate side was obtained by the same method as in Example 3. By observing the polymer membrane 4 by means of an electron microscope, it was

found that the pore diameter on the glass plate side was about 2 micrometers and the pore diameter on the side brought into contact with the nitrogen flow was about 0.01 micrometer. In addition, it was found by observation of the cross-section of the membrane that only an extremely thin layer on the side brought into contact with the nitrogen flow had pores of a small diameter. In addition, the separation factor of oxygen/nitrogen was 1.02.

EXAMPLE 5

Preparation of a polymerizable solution

A polymerizable solution 5 was obtained by altering the amount of methyl caprate (a non-solvent) in the polymerizable solution 3 of Example 3 to 80 parts.

Preparation of an asymmetric polymer membrane

An asymmetric polymer membrane 5 with a luster on the glass plate side and no luster on the side brought into contact with the nitrogen flow was obtained by the same method as in Example 3. Results of observations by means of an electron microscope were the same as those of Example 1. The separation factor of oxygen/nitrogen was 0.936.

EXAMPLE 6

Preparation of a polymerizable solution

A polymerizable solution 6 was obtained by mixing 60 parts urethane acrylate oligomer with a number average molecular weight of 3,000 and three acrylic groups on average per molecule, 20 parts 1,6-hexane diol diacrylate, 4 parts Irgacure-651 (a UV polymerization initiator manufactured by Ciba-Geigy Co., Ltd.), and 70 parts methyl caprate (a non-solvent).

Preparation of an asymmetric polymer membrane

A glass plate was coated with the polymerizable solution 6 by means of a film applicator so as to obtain a thickness of 200 micrometers. After keeping the glass plate under a nitrogen flow at 80 degrees C. for 3 seconds, the coating was irradiated with a UV ray having a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds by means of a metal halide lamp. It was observed that the coating film which was transparent before irradiation became opaque and white after irradiation. The obtained opaque white membrane was peeled off from the glass plate and the non-solvent, solvent, unreacted monomer and oligomer and the UV polymerization initiator were washed out by immersion in petroleum ether for 30 minutes. By thoroughly drying the membrane under a vacuum after cleaning, an asymmetric polymer membrane 6 with a luster on the side brought into contact with the nitrogen flow and no luster on the glass plate was obtained. Results of observations by means of an electron microscope were the same as in Example 4. In addition, the separation factor of oxygen/nitrogen was 0.936.

EXAMPLE 7

Preparation of a polymerizable solution

A polymerizable solution 7 was obtained by mixing 80 parts urethane acrylate oligomer with a number average molecular weight of 1,000 and three acrylic groups on average per molecule, 20 parts dicyclopentenyl acrylate, 4 parts Irgacure-651 (a UV polymerization initiator manufactured by Ciba-Geigy Co., Ltd.), 200

parts methyl caprate (a non-solvent), and 20 parts acetone (a solvent).

Preparation of an asymmetric polymer membrane

A polymer membrane 7 with a luster on the glass plate side and no luster on the side brought into contact with the nitrogen flow was obtained by the same method as in Example 1. By observing the polymer membrane 7 by means of an electron microscope, it was found that the pore diameter on the glass plate side was about 0.2 micrometer and the pore diameter on the side brought into contact with the nitrogen flow was about 5 micrometers. In addition, it was found from an examination of the cross-section that only an extremely thin layer on the glass plate side had pores with a small diameter. In addition, the separation factor of oxygen/nitrogen was 0.934.

COMPARATIVE EXAMPLE 1

The polymerizable solution 1 of Example 1 under a condition in which it was sandwiched between two glass plates with a spacer having a thickness of 200 micrometers was irradiated with a UV ray of a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds from a metal halide lamp. It was observed that the polymerizable solution which was transparent before irradiation became opaque and white after irradiation.

The obtained opaque white membrane was peeled off from the glass plate and was immersed in petroleum ether for 30 minutes to wash out the non-solvent, unreacted monomer and oligomer and the UV polymerization initiator. A polymer membrane 7 with no luster on both surfaces was obtained by thoroughly drying the membrane after cleaning under vacuum. By observing the polymer membrane 7 by means of an electron microscope, it was found that both faces had pore diameters of about 2 micrometers, and that the pore diameter was uniform in the thickness direction of the membrane, electron microscopic observation of a cross-section.

COMPARATIVE EXAMPLE 2

Using the polymerizable solution of Example 3, a polymer membrane 8 with no luster on both faces was obtained by the same method as in Comparative Example 1. Results of observations by means of an electron microscope were the same as those of Comparative Example 1.

COMPARATIVE EXAMPLE 3

A glass plate was coated with the polymerizable solution 6 of Example 6 by means of a film applicator so as to obtain a thickness of 200 micrometers. The glass plate was irradiated with a UV ray with a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds by means of a metal halide lamp. It was observed that the coating film which was transparent before irradiation became opaque and white after irradiation. The obtained opaque white membrane was peeled off from the glass plate and was immersed in petroleum ether for 30 minutes to wash out the non-solvent, unreacted monomer and oligomer and the UV polymerization initiator, resulting in a polymer membrane 9 with no luster on both faces. Results of observations by means of an electron microscope were the same as those of Comparative Example 1.

COMPARATIVE EXAMPLE 4

Preparation of a polymerizable solution

A polymerizable solution 7 was obtained by altering the fraction of the non-solvent methyl caprate in the polymerizable solution 6 of Example 6 to 60 parts.

Preparation of a polymer membrane

A polymer membrane 10 with luster on both faces was obtained by the same method as in Comparative Example 3. By observing the polymer membrane 10 by means of an electron microscope, it was found that both upper and lower faces each had pore diameters of about 0.01 micrometer, and the pore diameter was uniform in the thickness direction of the membrane by observation of a cross-section.

COMPARATIVE EXAMPLE 5

Preparation of a polymerizable solution

A polymerizable solution 8 was obtained by altering the fraction of the non-solvent methyl caprate in the polymerizable solution 6 of Example 6 to 80 parts.

Preparation of a polymer membrane

A polymer membrane 11 was obtained by the same method as that of Comparative Example 3. Results of observation by means of an electron microscope were the same as those for Comparative Example 1.

COMPARATIVE EXAMPLE 6

Preparation of a polymerizable solution

A polymerizable solution 9 was obtained by mixing 90 parts hydroxyethyl methacrylate, 10 parts ethylene glycol dimethacrylate, 4 parts Darocure-2959 (a UV polymerization initiator), 65 parts water, and 15 parts ethylene glycol.

Preparation of an asymmetric polymer membrane

Under a condition in which the polymerizable solution 9 was sandwiched between two glass plates having a spacer with a thickness of 400 micrometers, a lower glass plate was cooled to -40 degrees C. After the polymerizable solution 9 was frozen by cooling, a glass cell in which water at 20 degrees C was circulated was placed on the upper glass plate so as to melt the upper surface of the frozen polymerizable solution 9. Under this condition, the solution was irradiated with an ultraviolet ray with a wavelength of 360 nm and a strength of 100 mW/cm² for 10 seconds by means of a metal halide lamp positioned above the upper glass plate. Then, the obtained membrane was unfrozen and was peeled off from the glass plate to obtain an opaque white polymer membrane 12. By observing the polymer membrane 12 by means of an electron microscope, it was found that the upper face of the membrane had a pore diameter of 0.01 micrometer or less and the lower face of the membrane had a pore diameter of about 100 micrometers. In addition, it was found from the result of observation of a cross-section that the thickness of the part in which the pore diameter of the upper face of the membrane was 0.01 micrometer was about 5 micrometers.

Evaluation of filtration characteristics

On the polymer membrane 12, evaluation of filtration characteristics was impossible as a polyethylene glycol

aqueous solution did not pass through, even under a filtration pressure of 3 kg/cm².

In Examples 1 and 2, asymmetric polymer membranes were obtained by evaporation of diisobutyl ketone which was a non-solvent. In Examples 3, 4, and 5, asymmetric polymer membranes were obtained by evaporation of acetone and methyl isobutyl ketone which were solvents. In addition, in Example 6, phase separation on the surface of the membrane was not promoted by heating the surface of the membrane with a nitrogen flow at 80 degrees C. to obtain an asymmetric polymer membrane.

A polymer membrane with a pore diameter distribution in the cross-sectional direction of the membrane was not obtained in the Comparative Examples because in the Comparative Examples 1 and 2, evaporation of diisobutyl ketone did not occur as the polymerizable solution was sandwiched between glass plates and in Comparative Examples 3, 4 and 5, evaporation of non-solvent did not occur as the non-solvent was methyl caprate alone with a high boiling point.

It is clear from Table 1 that asymmetric polymer membranes in Examples 1-6 exhibited good filtration rates and molecular weight cut-off ability. In addition, the asymmetric polymer membrane in Example 7 could remove large substances with a diameter of 0.2 micrometer or larger and exhibited large filtration rates. The polymer membranes in Comparative Examples 1-5 which did not have a pore diameter distribution in the thickness direction of the membrane did not exhibit both excellent filtration rate and molecular weight cut-off ability at the same time. In addition, as is clearly shown in Comparative Examples 3, 4 and 5, even if the pore diameter of the membrane was controlled by changing the ratio of monomer and oligomer to non-solvent, it was impossible to obtain both excellent filtration rate and molecular weight cut-off ability at the same time.

In comparative Example 7, asymmetric polymer membranes were obtained; however, the dense layer was so thick that sufficient flux was not possible.

TABLE 1

	Flux (l/m ² · hr)	Rejection (%)
Example 1	25	80
Example 2	27	80
Example 3	30	89
Example 4	26	85
Example 5	35	80
Example 6	25	90
Example 7	30000	0
Comparative Example 1	28	35
Comparative Example 2	32	20
Comparative Example 3	33	50
Comparative Example 4	0	—
Comparative Example 5	250	0

What is claimed is:

1. A method for preparing an asymmetric polymer membrane having a pore diameter gradient in the depth

of the membrane, comprising the steps, in the following order, of:

providing a homogeneous polymerizable solution including at least one member of the group consisting of a monomer and an oligomer, the member forming a crosslinked polymer upon exposure to energetic radiation; and a solvent for the monomer or oligomer which does not dissolve and does not swell the polymer;

forming a layer of the homogeneous polymerizable solution;

evaporating a portion of the solvent from the layer of the homogeneous solution; and forming said polymers substantially solely by irradiating the layer of the homogeneous solution with energetic radiation.

2. A method for preparing an asymmetric polymer membrane having a pore diameter gradient in the depth of the membrane, comprising the steps, in the following order, of:

providing a homogeneous polymerizable solution including at least one member of the group consisting of a monomer and an oligomer, the member forming a crosslinked polymer upon exposure to energetic radiation; and a solvent for the monomer or oligomer which does not dissolve and does not swell the polymer;

forming a layer of the homogeneous polymerizable solution and

exposing the layer of the homogeneous solution to a temperature gradient while forming said polymers substantially solely by irradiating the layer of the homogeneous solution with energetic radiation.

3. A method for preparing an asymmetric polymer membrane as defined in claims 1 or 2, wherein the step of providing a homogeneous polymerizable solution further comprises including a second solvent which swells or dissolves the polymer.

4. An asymmetric polymer membrane comprising a polymer having a crosslinked structure formed by polymerizing at least one of a monomer and an oligomer polymerized substantially solely by exposure to radiation, the polymer membrane having continuous pores, a gradient of pore diameters from one face of the membrane to the opposing face of the membrane and a ratio of a permeability flux of oxygen to a permeability flux of nitrogen of 0.9-1.1.

5. An asymmetric polymer membrane as defined in claim 4 further comprising a porous, dense layer in the membrane including pores having the smallest diameters, the dense layer having a thickness of at most 5 μ m.

6. An asymmetric polymer membrane as defined in claim 4 further comprising a porous, supporting layer in the membrane including pores having the largest diameters, the largest pores having a diameter of 0.1 to 20 μ m.

7. An asymmetric polymer membrane as defined in claim 4, wherein the smallest pores have a diameter of 0.0005-0.015 μ m, whereby the polymer membrane has a molecular weight cut-off ability.

8. An asymmetric polymer membrane as defined in claim 4, wherein the smallest pores have a diameter of 0.2-20 μ m.

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United States Patent [19]
Miller

[11] **Patent Number:** **4,906,371**
 [45] **Date of Patent:** **Mar. 6, 1990**

[54] **FILTER ELEMENT HAVING
 MICROPOROUS MEMBRANE**

[75] **Inventor:** Matthew J. Miller, Cheshire, Conn.
 [73] **Assignee:** Cuno, Incorporated, Meriden, Conn.
 [21] **Appl. No.:** 339,928
 [22] **Filed:** Apr. 17, 1989

Related U.S. Application Data

[63] Continuation of Ser. No. 88,498, Aug. 17, 1987, abandoned, which is a continuation of Ser. No. 383,377, May 28, 1982, abandoned.

[51] **Int. Cl.:** B01D 13/00
 [52] **U.S. Cl.:** 210/321.61; 210/321.86;
 210/321.87; 210/485; 210/489; 210/493.2;
 210/497.01; 210/500.21
 [58] **Field of Search:** 210/433.1, 446, 448,
 210/485, 487, 489, 493.1-493.5, 497.1, 497.01,
 500.21, 503, 321.61, 505, 321.86, 321.87

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,415,384 12/1968 Kasten 210/492
 3,326,588 9/1970 Michaels 210/500.2

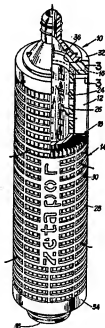
4,154,688 5/1979 Pall 210/487
 4,305,782 12/1981 Ostreicher et al. 210/505

Primary Examiner—Richard V. Fisher
Assistant Examiner—Wanda L. Millard
Attorney, Agent, or Firm—Weingram & Zall

[57] **ABSTRACT**

A filter element containing a hydrophilic nylon microporous filter membrane having a preformed substantially non-porous sealing area of non-porous tape heat sealed to the membrane and a filter housing having preferably a hydrophobic thermoplastic sealing surface in thermoplastic sealing relationship with the sealing area. Preferably, the filter membrane is a pleated cylindrical membrane and the housing includes endcaps thereto. The preferred pleated cylindrical membrane is produced from an elongated porous filtration area longitudinally bordered by the substantially non-porous sealing areas. Such a membrane may be produced by applying a heat sealable non-porous tape along the longitudinal borders of the filtration area. The filter element is particularly useful for the filtration of aqueous liquids, particularly parenteral or body liquids.

7 Claims, 2 Drawing Sheets



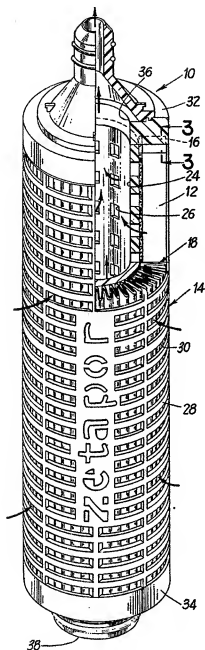


FIG. 1

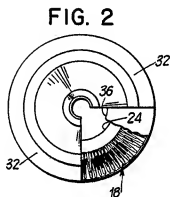
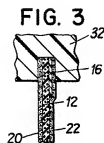
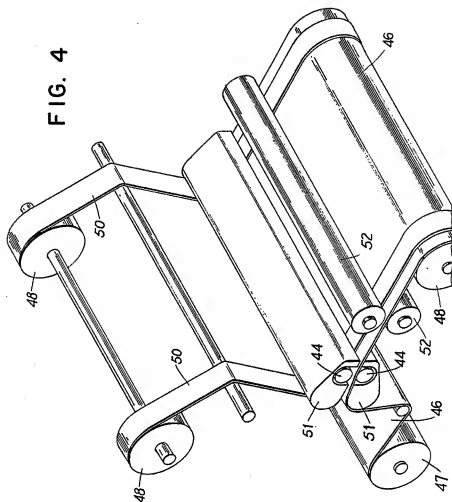


FIG. 4



FILTER ELEMENT HAVING MICROPOROUS MEMBRANE

This is a continuation of co-pending application Ser. No. 07/088,498 filed on 8/17/87, now abandoned, which is a continuation of Ser. No. 383,377 filed May 28, 1982, now abandoned.

RELATED APPLICATIONS

This application describes and claims a preferred subgenus of the generic invention described and claimed in U.S. Ser. No. 383,383 to Meyering et al, filed May 28, 1982 and now abandoned, the entire disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to filter elements utilizing hydrophilic microporous membrane as the filtration media, and more particularly to filter elements utilizing cylindrical pleated nylon membrane, said filter elements being suitable for the filtration of aqueous fluids, in particular parenteral or body liquids.

PRIOR ART

In many applications it is necessary to totally remove particles having dimensions in the submicrometer range. For this purpose, it is well known in the art to use a thin polymeric layer that is rendered highly porous with a substantially uniform pore size. Such layers are commonly termed microporous filtration membrane.

One characteristic of such microporous filter membrane is that they are extremely fragile and easily rupture when subjected to deformation due to rough handling, bending, or fluid pressure. Since even the most minute crack or break will destroy the effectiveness, it is necessary to use extreme care in manufacture and use.

Microporous filter membrane find many uses in industry, science and education. A common industrial application is the "cold" sterilization of pharmaceuticals and the stabilization of alcoholic beverages. In cold sterilization, the membrane has a sufficiently small pore size to block the passage of all bacteria present in the unfiltered fluid supplied to the upstream side. In the production of alcoholic beverages, the removal of bacteria, yeast and molds, stabilizes and clarifies the beverage. In the production of pharmaceuticals, the removal of bacteria is an essential step for obvious health reasons. In all of these applications it is essential that the filter membrane used be hydrophilic in order to filter such aqueous fluids.

There are many types of filter membranes available and processes for producing such membrane.

Nylon microporous filter membrane is well known in the art, for example, U.S. Pat. No. 3,876,738 to Marinaccio et al (1975) describes a process for preparing nylon microporous membrane by quenching a solution of a film forming polymer in a non-solvent system for the polymer. European Patent Application 0 005 536 to Pall (1979) describes a similar type process for producing nylon membrane.

Other type polymeric microporous membranes, including nylon and processes for producing such membranes are described, for example in the following U.S. Pat. Nos.:

3,642,668 to Bailey et al (1972);
4,203,847 to Grandine, II (1980);
4,203,848 to Grandine, II (1980); and

4,247,498 to Castro, (1980).

Commercially available nylon microporous filter membranes are available from Pall Corp., Glen Cove, N.Y., under the trademark ULTIPOR N₆₅ and N₆₆ POSIDYNE. Another commercially significant filter membrane made of polyvinylidene fluoride is available from Millipore Corp., Bedford, Mass., under the trademark DURAPORE. This membrane is probably produced by the aforementioned Grandine, II patents.

Additionally, the Assignee of this application is selling cationically charged modified nylon microporous filter membrane under the trademark ZETAPOR. These membranes are described and claimed in U.S. Ser. No. 268,543 filed on May 29th, 1981 to Barnes et al, now U.S. Pat. No. 4,473,475; and U.S. Ser. No. 314,307 filed on Oct. 23, 1981 to Ostreicher et al, now U.S. Pat. No. 4,473,474. Barnes et al describes the use of charged modified membrane for the filtration of high purity water (18 megohmcentimeter resistivity) used in the electronics industry; and Ostreicher et al describes the use of charged modified membrane for the filtration of parenteral or body liquids. Additionally, it should be noted that these filter membranes are typically reinforced by various means. A unique method of reinforcement is described in the Assignee's U.S. Ser. No. 332,068, filed Dec. 18, 1981 to Barnes et al, now abandoned.

All of the aforementioned membranes, besides being used in sheet form, are used in various type filter elements. Generally, the filter element comprises the filter membrane and a filter housing with a sealing surface in sealing relationship with a sealing area of the membrane. A well known type filter element is the pleated cartridge type filter element described, for example, in U.S. Pat. No. 3,457,339 to Pall et al (1969). Another well known type of filter element is the hermetically sealed intravenous unit described in U.S. Pat. No. 4,113,627 to Leason (1978).

In the critical applications for such filter elements, it is imperative that the filter membrane not be damaged during production and that the filtrate not bypass the filter membrane. Either situation could be catastrophic, for example, allowing contaminants to enter the blood stream of a patient. It is therefore necessary that an undamaged seal exist between the sealing area of the membrane and the sealing surface of the filter housing to prevent leakage around the filter membrane. In order to insure such integrity, the filter element is "integrity tested" to insure the integrity of the filter element. This is generally accomplished by a "bubble point" test of the filter element by methods well known in the art. A particular type of integrity testing device for filter cartridges is commercially available under the name ZETAWATCH, from AMF Cuno Division, Meriden, Conn. and described and claimed in the Assignee's co-pending U.S. Ser. No. 265,481, filed May 20, 1981, to Kowalski, now U.S. Pat. No. 4,384,474. This integrity tester is self contained and electrically monitors the individual cartridge elements's integrity within a multiple cartridge housing. Other methods of such integrity testing are described in "Non-Destructive Test For Bacterial Retentive Filters" by Ben Trasen which was published in the Sept./Oct. 1979 issue of the Journal of Parenteral Drug Association, pages 273-2798. All of the known integrity tests require a thorough wetting of the membrane and sealing surfaces associated therewith to provide an accurate determination of integrity. If the filter membrane is broken, even microscopically, if the

membrane is improperly installed, or if the membrane sealing surfaces are not completely wetted, bubbles will appear immediately at the point of the break or leak.

Additionally, any filter element must, particularly when used to filter parenteral or biological liquids, have a minimum of extractable contaminants introduced into the filtrate. These contaminants may be harmful toxins when introduced into a patient. Specifically, any filter element must meet the test standards of the industry, e.g. ASTM D-3861-79.

Still further, filter elements used to filter parenteral or biological liquids should be heat sterilizable and autoclavable, without deterioration or discoloration of the housing or membrane or deterioration of the seal between the membrane and housing. A preferred housing material is polypropylene which is hydrophobic.

Several methods of sealing filter elements have been employed in the past. These methods include pressure clamping, heat sealing, ultrasonic welding, adhesive and solvent bonding, and injection molding. These prior art methods fail to provide on occasion the 100% positive seal which is necessary to prevent leakages. In particular where microporous filter membranes are used in the filter element, there is some danger when using these methods that the delicate filter media will be damaged during the sealing process.

Known methods of pressure clamping and other mechanical interlocking systems tend to distort the filter membrane or actually damage the membrane at the clamping edges, thereby destroying the integrity of the membrane and allowing contaminants to pass through. Also conditions such as time, and heat stress relieving can allow the pressure seal to relax. Additionally, this method is particularly complicated when a pleated filter cartridge is assembled. Known methods of heat sealing, sonic welding and related thermomechanical bonding methods may also damage the filter membrane at the sealing edges. The use of adhesives or solvent bonding has disadvantages in that another material is introduced into the filter element that can lead to extractable contaminants. Often the constituents of an adhesive or solvent system may also damage the filter membrane.

The foregoing methods of sealing the filter housing to a filter membrane are particularly troublesome when a hydrophobic sealing surface is in contact with a hydrophilic sealing area. This is often the case when the filter element is used to filter biological or parenteral liquids where it is very highly desirable to use a polypropylene housing (which is resistant to autoclaving and heat sterilization) and undesirable to use adhesives or solvents for sealing (to avoid high extractables). For such elements, the housing is usually thermoplastically sealed to the membrane, increasing the chances for damage to the sealing areas of the membrane. Additionally, it appears that the hydrophobic sealing surface of the housing in contact with the porous hydrophilic sealing area of the membrane increases the chances that the filter element will not pass industry integrity tests. This is probably brought about by the incomplete wetting of the membrane/housing interface which gives a reduced bubble point. For example, it has been found that in the thermoplastic sealing of polypropylene end caps to cylindrical pleated nylon membrane filter cartridges, an unacceptably low percentage of the cartridges passed the industry integrity test.

More specifically, the following prior art references are relevant to the invention described and claimed herein.

U.S. Pat. No. 1,476,392 to Carroll (1923) describes a process of making a composite film by casting a plastic or flowable cellulosic material, e.g. cellulose acetate, on to a moving wheel from a plurality of compartments to thereby produce a plurality of adjacent film strips. This reference does not teach or suggest the production of a microporous filter membrane.

U.S. Pat. No. 2,663,660, to Layte (1953) describes a method of assembling filter elements, e.g. a filter cartridge, by producing an elongated strip of filter paper and folding elongated tapes of adhesive material on the elongated edges. The filter paper is then cut to size and pleated transversely of the length of the strip, and rolled into an annulus form. The outer portions of the adhesive tape material is then moistened with a suitable solvent material for the adhesive at the ends of the annulus are formed and thereafter the ends of the annulus are capped by end caps. The end caps are preferably heavy cardboard. Layte does not teach or suggest the use of such a method in conjunction with microporous membrane nor is such a method suitable for producing filter cartridges for filtering parenteral or biological liquids wherein extractables must be minimized.

U.S. Pat. No. 3,013,607, to Jackson et al (1961) relates to a method of end capping tubular filter elements of paper, cardboard, felt, woven tissue, etc. Thermoplastic end caps are subjected to heat induced in the field of an electric inductance coil in contact with the cap, to a point where the cap is softened so that the edges of the filter can be embedded in the cap to the depth required to bind the parts together. A metallic strip is applied to the edges of the filter and external support jacket, or the edges of the filter element and external support jacket are coated with an electrically conductive or semiconductive material, so as to reinforce the filter edges, and enhance the heat conduction through the edges and end cap. Jackson et al does not utilize an organic polymeric microporous filter membrane and thus does not recognize the problems associated with the integrity testing of filter elements containing such hydrophilic membrane in conjunction with a hydrophobic end cap.

Additionally, the use of a metallic strip on the edges of the Jackson et al filter limits greatly the application to which the end capped filter elements can be put. For example, under certain conditions, the metallic strip can corrode and/or contaminate the material being filtered or the medium being filtered. Such a filter element is completely unacceptable for the filtration of biological and parenteral liquids. Still further the use of such a metallic strip on the edges of the filter elements increases the cost of making the filter elements, and complicates the procedure used in corrugating such filter elements.

U.S. Pat. No. 3,407,252 to Pall et al (1968) describes the production of a corrugated or pleated filter media in annulus form which utilizes a ribbon or tape of bonding agent such as a heat sealable and curable epoxy resin, to form a leak-proof seal along the longitudinal meeting of the pleated filter media.

U.S. Pat. No. 3,457,339 to Pall et al (1969) describes a process for applying preformed end caps to filter sheet material, particularly sheet materials formed of fiber and in substantially tubular shape. The process involves heating the inside face of the thermoplastic end cap to fuse a portion of the cap into a liquid. The liquid is of a viscosity which is capable of penetrating through the pores of the filter sheet. The edges of the cylindrical sheet are then embedded in the liquidified end cap so that the liquidified thermoplastic material penetrates

through the pores of the embedded portions of the filter sheet material from one surface to the other. The liquid plastic is then hardened and said to form a substantially continuous leak proof matrix of end cap material permeating through the pores of the filter material and bonding the filter sheet to the end cap in a leak proof seal.

This process for applying end caps to a filter sheet has the advantage in that it does not require the use of adhesives. If this Pall et al process, however, is utilized using end caps of a hydrophobic material, and a hydrophilic membrane, an excessive percentage of the cartridges do not pass the industry integrity test. It is believed that this is due to the cartridge not being completely wetted at the interface between the hydrophilic membrane and the hydrophobic end cap. Hydrophobic type end caps may be utilized if the cartridge is integrity tested in a non-aqueous solvent. This, however, limits the application of the filter element. If a hydrophilic type end cap, e.g. polyester, is used, the cartridge will generally have inferior solvent and chemical resistance and inferior resistance to autoclaving and heat.

This Pall et al process requires that the sealing areas of the filter sheet material be porous to permit penetration of the liquified thermoplastic material through the pores of the embedded portion of the filter sheet material from one surface to the other. Additionally, during prosecution Pall et al states:

"... The instant process is simple enough to enable rapid manufacture of filter elements with a minimum of manufacturing steps and without the necessity of employing bonding agents and components other than the actual materials of the filter and end cap..."

In effect Pall et al teaches away from Applicant's invention which utilizes a substantially non-porous sealing area and which utilizes other components than the actual materials of the filter and end cap.

U.S. Pat. No. 3,471,019 to Trasen et al (1969) describes a filter unit comprised of a two-part housing provided with sealing portions adapted to be aligned with each other and with a peripheral portion of the filter completely surrounding the central portions of the filter. In assembly of the unit, the sealing portions of the housings are pressed against the opposite sides of the filter and the sealing portion of at least one of the parts of the housing is heated to cause the material thereof to melt and flow through the aligned pores of the peripheral portions of the filter and fused to the sealing portion of the other part of the housing. A similar type filter and sealing method is described in U.S. Pat. No. 3,782,083 to Rosenberg (1974) wherein the plastic material runs through the pores of the filter element forming a fluid tight integral seal closing all sides of the element to fluid flow.

U.S. Pat. No. 3,487,943 to Buckman (1967) describes a filter element made of pleated filter paper. One portion of the filter element is modified so that in operation of the filter the liquid flow velocity through the modified portion is less than that through the remainder of the element. The modified portion may be formed by compressing together a series of pleats or by sealing to a group of pleats on one side of the element a sheet of similar or dissimilar filter material. The similar or dissimilar filter material is sealed to the annulus cartridge over the inner or outer periphery of the cartridge and does not form a continuous edge along the top of the filter near the end cap.

U.S. Pat. No. 3,591,010 to Pall et al (1971) describes a corrugated element having a microporous layer deposited on a substrate sheet provided with portions of reduced porosity at the areas of the base folds of the corrugations.

U.S. Pat. No. 3,815,754 to Rosenberg (1974) describes a box filter wherein the elements of the filter housing are bonded to the filter sheet by fused integration of the housing members through the open pores of the filter element, forming a fluid tight seal all along the sides of the filter sheet. Such a bond is obtained by, for example, ultrasonic welding, solvent softening or heat fusion.

U.S. Pat. Nos. 3,865,919 and 3,867,294 to Pall et al (1975) describe cylindrical elements having an improved side seam seal which can be bonded to end caps in a leak type manner.

U.S. Pat. No. 3,954,625 to Michalski (1976) describes a filter which includes a plastic housing and an intermediate filter screen. The peripheral portion of the screen is sealed between the two housing halves by flowing a portion of at least one of the housing halves through the screen and bonding that portion to the other housing half.

U.S. Pat. No. 4,101,423 to Merrill et al (1978) describes a tubular filtration element whose ends are impregnated with a suitable sealing adhesive. When the adhesive material cures, the end portion provides mechanical support for the tube and blocks the passage of the fluid or the particulate and bacterial contaminant. Merrill et al requires that the sealing material used to form the ends must be hydrophilic when cured, stating:

"If the sealant rendered the filter adjacent to it hydrophobic, the filter would not be wetted and would not then offer capillary resistance to the bubble point test gas, therefore the bubble point could not be used as an indication of filter integrity..." (Col. 9, lines 59-64).

"It will be understood that if the outer layer (of the filter) is formed from a lacquer impregnated paper, the resilient members can safely apply a sealing force sufficient to block the fluid from the end portions so that a hydrophobic sealing material may be used." (Col. 10, lines 6-10).

The filtration element is supported and sealed within a housing by radial seal force, i.e. the filtration element and housing are not in thermoplastic sealing relationship to each other.

U.S. Pat. No. 4,154,688 to Pall (1979) describes the use of thermoplastic end cap applied to the open ends of a filtered tube in accordance with the aforementioned U.S. Pat. No. 3,457,339 to Pall et al.

U.S. Pat. No. 4,193,876 to Leeke et al (1980) describes dryforming the peripheral portion of discs of filter media, particularly filter media containing non-compressible particulate to suppress edge leakage in filter presses.

In assignee's U.S. Ser. No. 253,345 to Southall, filed Apr. 13, 1981, now U.S. Pat. No. 4,347,208, a method is described of making a filter cell comprised of two cellulosic fiber containing filter media having a sealed periphery. The method comprises compressing the periphery of each filter media to form a flange. The media are then aligned to provide intimate face to face contact between the flanges and a spacer means provided between the media to cause each to distal outwardly from the other media. The media and spacer means are then placed into a mold surrounding the flanges. The mold has a means for providing a recompression force to the

inner portions of the flanges. A thermoplastic polymer is then injected into the mold to form a seal around the flanges.

Additionally, MICRO-SCREEN filter cartridges are commercially available from AMF Cone Division, Meriden, Conn., comprising a stainless steel pleated cylindrical screen welded to stainless steel end caps. Shim stock is welded to the screens at both ends to effectively seal off the end so that the end caps can be welded thereon without destroying the filter screen thereunder.

Still further, DURAPORE TP filter cartridges have of recent date become commercially available from Millipore Corp., Bedford, Mass. This cartridge comprises a polyvinylidene fluoride pleated cylindrical membrane fused to polypropylene end caps. Nonporous polypropylene tape is laminated to the ends of the membrane cylinder prior to pleating. The tape is apparently adhered to the membrane by partial dissolution with a solvent of the tape and/or membrane and application of sufficient pressure to the tape to mechanically bind them together. The solvent is then removed by evaporation.

In summary, in most of the prior art uncovered by applicant relating to sealing filters, the filter media sealing area is porous, so that when a thermoplastic or sealing surface is applied thereto it flows through the porous media to effect the seal. Other prior art utilizes solvents and solvent adhesives for sealing which can increase extractable contaminants (an undesirable condition when filtering parenteral or biological liquids) and damage, for example, the nylon membrane pore structure.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of this invention to provide a filter element which has an effective thermoplastic seal between a hydrophilic nylon membrane and the hydrophobic surface of the filter housing.

It is a further object of this invention to provide an effective seal without the use of adhesives.

It is still a further object of this invention to provide a filter element which is particularly useful for the filtration of aqueous fluids, in particular biological and parenteral liquids.

It is yet another object of this invention to provide a filter element comprising a fragile nylon microporous filter membrane in cylindrical form which has reinforced ends permitting the ends to be embedded in a softened thermoplastic end cap without damage to the ends and/or sealing integrity of the filter element.

It is still another object of this invention to provide a filter membrane for use in the filter element of this invention.

It is a further object of this invention to provide novel processes for producing the filter elements and filter membranes of this invention.

In accordance with the present invention, a filter element is provided which comprises:

(a) a hydrophilic nylon microporous filter membrane having a preformed substantially non-porous sealing area of non-porous tape heat sealed to the membrane; and

(b) a filter housing having a hydrophobic thermoplastic sealing surface in thermoplastic sealing relationship with the sealing area.

Preferably the filter membrane is in cylindrical form having the non-porous sealing areas at each end of the cylinder and the housing having an end cap at each end of the cylinder.

The filter membrane used in the aforementioned preferred filter element comprises an elongated porous filtration area longitudinally bordered by the substantially non-porous sealing areas. This filter membrane used may be produced by preparing the filter membrane by known methods and then applying the heat sealable non-porous tape along the longitudinal borders of the filtration areas.

The filter elements of this invention are useful for the filtration of aqueous liquids, particularly parenteral or body liquids.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view, partially broken away, of a preferred filter element of this invention.

FIG. 2 is a top view, partially in section, of the filter element of FIG. 1.

FIG. 3 is an enlarged view in section, taken along line 3-3 of FIG. 1 depicting the sealing surface between the membrane and filter element.

FIG. 4 is a schematic perspective of an apparatus that may be used to prepare a filter membrane by applying a non-porous tape along the longitudinal borders of the filtration area.

DETAILED DESCRIPTION OF THE INVENTION

FIGS. 1 through 3 depict a preferred embodiment of the filter element of this invention. The filter element, generally designated (10) is comprised of the nylon filter membrane (12) and the filter housing, generally designated (14). The filter membrane is in cylindrical form having the substantially non-porous area of heat bonded non-porous tape (16) at each end of the cylinder (18). Referring to FIG. 3, the filter membrane (12) is sandwiched between inner and outer layers (20) and (22) of, for example, polypropylene woven netting.

The composite of filter membrane (12) and inner and outer layers (20 and 22) is pleated transversely to its length and formed into cylinder (18). The cylinder (18) is then slipped over a foraminous cylindrical core (24) which is provided with apertures (26) for flow into the open interior of the core (24). The filter membrane (12) and core (24) are then slipped into an outer cylindrical member (28) which is also provided with apertures (30). The ends of the cylinders are then capped by end caps (32 and 34).

The end caps (32 and 34) are sealed by thermoplastic fusion to the non-porous areas (16) of the filter membrane (12). The end caps (32 and 34) close off the interior from the exterior of the filter element. The fluid can thus flow from the outside to the interior of the filter element, since interior and exterior are completely separated by the filter element and sealed off by the end caps (32 and 34). The end caps (32 and 34) each have a central aperture (36 and 38).

The preformed end caps (32 and 34) are preferably applied to the cylindrical membrane (18) by heating an inside face of the thermoplastic end cap to a temperature sufficient to soften and preferably not liquify, a sufficient amount of the end cap to form a thermoplastic seal with the non-porous area at each end of the cylinder. All of the edges of one end of the cylinder are then embedded into the softened end cap. The softened end

cap material is then hardened, typically by cooling at ambient conditions, to form a thermoplastic sealing relationship between the sealing surface of the end cap and non-porous area thereby forming a leak proof seal.

A method of applying end caps to filter elements is described in the aforementioned U.S. Pat. No. 3,457,339 to Pall et al. Such a method and apparatus described therein may be modified to apply end caps in this invention. The major differences between the method used in this invention and the Pall et al method, is that Pall et al liquifies a portion of the end cap which permeates through the porous sealing surface of the filter membrane; whereas Applicants do not require the end cap to be liquified and, as clearly indicated herein, the sealing surface of the membrane is non-porous.

End caps of thermoplastic materials are preferred because of the ease of bonding, but it is also possible to use thermosetting resins in a thermoplastic, fusible or heat softenable stage of polymerization, until bonding has been effected, after which the curing of the resin can be completed to produce a structure which can no longer be separated. Such a structure is autoclavable without danger destroying the fluid tight seal between the housing portions and the filter membrane and the end caps. Thermoplastic resins whose softening point is sufficiently high so that they are not softened under sterilizing autoclaving conditions are preferred for medical use. Exemplary of the plastic materials which can be used are polyolefins (polyethylene, polypropylene, polybutylene, polyisobutylene), polyamides, polyvinylchloride, polyvinylidene chloride, polycacrylonitrile, polyesters, polycarbonates, polymethacrylate, polyallyl, and polyoxymethylene resins. Polytetrafluorethylene and polytrifluorochloroethylene can also be used. Polypropylene is preferred for the filtration of biological and parenteral liquids in that it can withstand autoclaving and sterilizing without discoloration or distortion. Other type materials, which may be hydrophilic, are generally unsuitable for such uses due to discoloration, distortion, etc. caused by the autoclaving and sterilization, however they may be used in conjunction with the membrane of this invention for other uses.

The hydrophilic nylon microporous filter membranes used in the filter element of this invention are well known in the art.

By the use of the term "microporous membrane" as used herein, it is meant a porous single layer, multiple layer or reinforced single or multiple layer membrane, having an effective pore size of at least 0.1 microns or larger or an initial bubble point (IBP) in water of less than 90 psi. A maximum pore size used for such membrane is about 1.2 microns or an IBP of greater than 8 psi. Preferably, but not necessarily, a single layer membrane is substantially symmetrical and isotropic. By "symmetrical", it is meant that the pore structure is substantially the same on both sides of the membrane. Asymmetric membranes, i.e., membranes having one side formed with a very tight thin layer which is supported by a more porous open structure, may also be utilized in this invention. By the use of the term "isotropic", it is meant the membrane has a uniform pore structure throughout the membrane.

The microporous nylon membranes used in this invention are hydrophilic. By the use of the term "hydrophilic", in describing the membranes, it is meant a membrane which adsorbs or adsorbs water. Generally, such hydrophilicity is produced by a sufficient amount of hydroxide (OH-) carboxyl (-COOH), amino (NH₂)

and/or similar functional groups on the surface of the membrane. Such groups assist in the adsorption and/or absorption of the water onto the membrane, i.e. "wetting out" of the membrane. Such hydrophilicity is preferable in the filtration of aqueous fluid.

The term "nylon" is intended to embrace film forming polyamide resins including copolymers and terpolymers which include the recurring amide grouping.

While, generally, the various nylon or polyamide resins are copolymers of diamine and a dicarboxylic acid, or homopolymers of a lactam and an amino acid, they vary widely in crystallinity or solids structure, melting point, and other physical properties. Preferred nylons for use in this invention are copolymers of hexamethylene diamine and adipic acid (nylon 66), copolymers of hexamethylene diamine and sebacic acid (nylon 610), and homopolymers of poly- ϵ -caprolactam (nylon 6). Alternatively, these preferred polyamide resins have a ratio of methylene (CH₂) to amide (NHCO) groups within the range about 5:1 to about 8:1, most preferably about 5:1 to about 7:1. Nylon 6 and nylon 66 each have a ratio of 6:1, whereas nylon 610 has a ratio of 8:1. The nylon polymers are available in a wide variety of grades, which vary appreciably with respect to molecular weight, within the range from about 15,000 to about 42,000 (number average molecular weight) and in other characteristics.

The highly preferred species of the units composing the polymer chain is polyhexamethylene adipamide, i.e. nylon 66, and molecular weights above about 30,000 are preferred. Polymers free of additives are generally preferred, but the addition of antioxidants or similar additives may have benefit under some conditions.

The preferred nylon microporous membranes are produced from nylon by the method disclosed in U.S. Pat. No. 3,876,738 to Marinaccio et al. Another method for producing such membranes is described in European Patent Application No. 0 005 536 to Pall. The entire disclosures of both of these references are incorporated herein by reference.

Both of these methods for producing nylon microporous membranes may be described as "quench techniques", i.e. casting or extruding a solution of a film forming polymer onto a substrate and quenching the cast film.

Broadly, Marinaccio et al produces microporous membrane by casting or extruding onto a substrate a casting solution of a film-forming polymer in a solvent system and quenching in a bath comprised of a nonsolvent system for the polymer.

The aforementioned Pall application describes another similar method which may be used for the conversion of nylon polymer into nylon microporous membrane. Broadly, Pall provides a process for preparing skinless hydrophilic alcohol-insoluble polyamide resin from a polyamide casting solution. The casting solution is formed by inducing nucleation of the solution by the controlled addition of a nonsolvent for the polyamide resin to obtain a visible precipitate of polyamide resin particles.

The casting solution, e.g. whether that of Marinaccio et al or Pall, is then spread on a substrate, i.e. reinforcing web or non-porous substrate, to form a thin film thereon. The cast film is then contacted with the quenching bath comprised of a non-solvent system for the polymer for a time sufficient to form micropores in the film. The preferred quench bath for forming a nylon

microporous membrane comprises a nonsolvent system of methanol and water or formic acid and water.

These preferred nylon membranes, i.e. described in Marinaccio et al and Fall, are characterized by an isotropic structure, having a high effective surface area and a fine internal microstructure of controlled pore dimensions with narrow pore size distribution and adequate pore volume. For example, a representative 0.22 micron rated nylon 66 membrane (polyhexamethylene adipamide) exhibits an Initial Bubble Point (IBP) of about 45 to 50 psid, a Foam All Over Point (FAOP) of about 50 to 55 psid, provides a flow of from 70 to 80 ml/min of water at 5 psid (47 mm. diameter discs), has a surface area (BET, nitrogen adsorption) of about 13 m²/g and a thickness of about 4.5 to 4.75 mils.

In general, nylon microporous filter membranes are be cast at thicknesses in the range of from about 1 mil to about 20 mils, preferably from about 1 to about 10 mils (wet thickness). After the polymer solution is cast and quenched, the membrane is removed from the quench bath and substrate upon which it was cast and then washed.

The washed membrane is then, preferably, laminated to another washed membrane, or optionally laminated to a web by methods well known in the art, to form a reinforced laminated filtration membrane. A unique reinforced membrane is described and claimed in U.S. Ser. No. 332,068 to Barnes et al filed Dec. 18, 1981, now abandoned, the entire disclosure of which is incorporated herein by reference. Preferably, lamination is accomplished by passing the plurality of layers juxtaposed upon each other through heated rollers to heat laminate and dry the membranes together. Preferably such drying is under restraint to prevent shrinkage. Drying of the membranes under restraint is described in the Assignee's copending U.S. Ser. No. 201,086 to Repetti, filed Oct. 27, 1980, now abandoned. The entire disclosure of this application is incorporated herein by reference. Generally, any suitable restraining technique may be used while drying, such as winding the membrane tightly about a dry surface, e.g. a drum. Biaxial control is preferred and tensioning the laminated membrane is considered the most preferred.

The final drying and curing temperature for the filtration membrane should be sufficient to dry and cure the membranes. Preferably this temperature is from about 120° C. to 140° C. for minimization of drying time without embrittlement or other detrimental effects to the membranes. The total thickness of the filtration membrane is preferably from about 3 mils to about 30 mils and most preferably about 5 to 15 mils thick (dry thickness).

The filtration membrane may then be rolled and stored under ambient conditions for further processing. Preferably, after formation of the membrane but prior to forming the membrane into the filtration membrane of this invention, it may be treated in accordance with U.S. Ser. No. 314,307, filed Oct. 23, 1981 to Ostreicher et al, now U.S. Pat. No. 4,473,474, to produce a cationically charged modified microporous membrane particularly suitable for the filtration of parenteral or biological liquids; or in accordance with U.S. Ser. No. 268,543, filed May 29, 1981 to Barnes et al, now U.S. Pat. No. 4,473,475, to produce another type cationically charged modified microporous membrane, particularly suitable for the filtration of high purity water, i.e. at least 18 megohm-cm resistivity, required in the manufacture of

electronic component. The entire disclosures of both of these applications are incorporated herein by reference.

The preferred form of the nylon filter membrane is an elongated porous filtration area bordered by substantially non-porous sealing areas of non-porous tape heat sealed to the membrane. This membrane is then pleated transversely to its length and formed into cylinder. It has been found that the objects of this invention may be achieved by application of the tape to only one face of the membrane, although the tape may be applied to both faces.

In order to produce this preferred form of the filter membrane, the apparatus of FIG. 4 may be utilized. The apparatus broadly comprises a pair of laminating rollers (44) through which the nylon microporous membrane (46) passes, supplied from roller (47). The membrane may be produced by any of the methods well known in the art, preferably by the aforementioned Marinaccio et al process. Tape supply rollers (48) feed non-porous tape (50) across heat shoes (51) and along the longitudinal borders just prior to the entrance of the membrane (46) into rollers (44). The heat shoes (51) are heated to temperatures which are sufficient to soften the solventless adhesive applied to the underside of tape (50) and allow bonding of the tape to the membrane (46) upon cooling. Such temperatures depend upon the specific nylon used, the tape, tape thickness, adhesive, etc. The shoes (51), in order to more accurately control the process and prevent damage to the membrane, may each be individually heated to different temperatures. Rollers (44) apply forces along the longitudinal borders of the membrane to heat seal the tape (50) to the borders of the membrane (46). The membrane (46) is then conveyed through pull rollers (52) to take up roller (48). An apparatus which has been found to be particularly suited for such procedure is a modified Model No. 25 from Laminex, Inc., Mathews, N.C. The apparatus is modified to accept two tape feed rollers (48) rather than a single roller the full width of the apparatus.

By the use of the term "heat sealable . . . tape" it is meant a tape which can be heat sealed on one surface to a nylon membrane substrate. Preferably, the tape is coated with a solventless melt adhesive which melts at a temperature which is lower than the melt temperature of the tape material or nylon membrane, and which upon cooling, is capable of bonding the tape to the nylon membrane. The solventless hot melt adhesive should not have such a low melt temperature that it will not adhesively function at typical heat sterilization and autoclave temperatures, e.g. above about 100° C. Such hot melt adhesives are, for example, polyamides and polyolefin type adhesives. A preferred adhesive is polyethylene.

Preferably the tape utilized is a polyester type tape, however, any polymeric tape may be utilized which is non-porous, can withstand the temperatures of use, autoclaving and sealing and does not produce detrimental extractables. Other tapes suitable for such use are polyamides, polyolefins etc. A commercially available and preferred tape having a hot melt adhesive thereon is sold under the trademark PERMALAM 150 by Laminex Inc. and is a polyester tape having a solventless hot melt adhesive of polyethylene. When using this specific tape the heat shoe in contact with the membrane is heated to about 200° F. (93° C.) and the heat shoes in contact with the tape is heated to about 300° F. (149° C.).

Scanning Electron Micrographs of the sealing area of the membrane produced by heat sealing the polyester tape to the borders of the membrane indicate that the tape completely blocks the surface pores of the membrane without significant penetration into the porous membrane. Thus the tape prevents entry into the pores by the softened material of the end cap which is subsequently applied and reinforces the membrane, thus decreasing the opportunity for degradation of the membrane by heat and mechanical stress during production. 10

The filter element of this invention can thus utilize the preferred hydrophobic filter housing, e.g. polypropylene, is simple and economical to manufacture, and has no solvents employed in manufacturing to adhere the tape to the membrane or the filter housing to the membrane. The tape also adds to the structural rigidity of the membrane.

For so called sterile filtrations, involving biological liquids, the filter element is sanitized or sterilized by autoclaving or hot water flushing prior to use. The filtration element and membrane of this invention are resistant to this type treatment, and retain their integrity under such conditions. Additionally, the filter element of this invention can withstand numerous wetting and drying cycles and high forward flow (FIG. 1) and reverse flow (not shown) pressures without failure.

What is claimed is:

1. A filter cartridge for filtration of aqueous liquids comprising:

- (a) at least one end cap having a sealing surface made of hydrophobic thermoplastic material;
- (b) a hydrophilic microporous nylon membrane in sheet form and having at least one edge;
- (c) a netting layer on at least one side of said membrane;

(d) a non-porous heat-sealing tape extending along said at least one edge of said membrane and bonded thereto;

(e) said membrane and netting layer being folded to form a pleated filtering surface;

(f) said tape forming a sealing layer along at least one peripheral end of said filtering surface and being partially embedded and thermoplastically sealed within said sealing surface of said end cap; and

(g) said tape substantially blocking micropores on said edge of said hydrophilic membrane to minimize adsorption of hydrophobic thermoplastic material along said peripheral end of said filtering surface during a thermoplastic sealing process when the filter cartridge is manufactured, so that aqueous liquids to be filtered can thoroughly and completely wet said hydrophilic membrane along said peripheral end of said filtering surface.

2. A filter cartridge as claimed in claim 1 wherein said tape extends along opposing edges of said membrane.

3. A filter cartridge as claimed in claim 1 wherein said filter cartridge further comprises a filter housing in the form of a cage which structurally encloses said membrane.

4. A filter cartridge as claimed in claim 1 wherein said tape comprises a melt adhesive which is polyethylene.

5. A filter cartridge as claimed in claim 1 wherein said membrane has a pore size of about 0.2 to about 0.85 microns.

6. A filter cartridge as claimed in claim 1 wherein said netting layer is on both sides of said membrane.

7. A filter cartridge as claimed in claim 1 wherein said tape is disposed between said membrane and netting layer.

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